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Supporting Information

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Direct Top-Down Fabrication of Large-Area Graphene Arrays by an In Situ Etching Method

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Direct Top-Down Fabrication of Large-Area Graphene Arrays by In-Situ Etching Method

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Methods:

50 μm thick Cu foil (99.8% purity) and 100 μm thick W foil (99.95%) were obtained from Alfa Aesar. Several pieces of Cu foils were placed on the W substrate. After samples were put into the 1 inch quartz tube, the whole system was pumped to ~5 Pa followed by filling the system with H_2. After switching off pumping, the quartz tube is at an ambient pressure with continuous H_2 flow. The furnace was then heated up to a fixed temperature in ~1 h followed by annealing the substrates for 50–60 min. The growth and etching parts are described in the main text.

Etched-left hexagonal graphene flakes were transferred to a 300 nm SiO_2/Si substrate by electrochemical method. The samples were characterized by scanning electron microscopy (SEM, Hitachi S-4800, 1 kV), TEM (Tecnai G2 F20 U-TWIN Transimission Electron Microscope operated at 200 kV), and Raman spectroscopy (Renishaw inVia Plus, with laser excitation at 514 nm).

Table S1. Summary of growth and etching conditions for graphene film and crystals, respectively.

Graphene type	Stage	Temperature (°C)	CH_4 (sccm)	Ar (sccm)	H_2 (sccm)	Time (min)
Film	Growth	1140	0.7	1500	30	60
	Etch	1140	0	1500	20	120
Crystals	Growth	1140	0.7	1500	30	40
	Etch	1140	0	1500	20	60

Table S2. Etching conditions for effects of graphene etching mode.

Etching mode	Stage	Temperature (°C)	CH_4 (sccm)	Ar (sccm)	H_2 (sccm)	Time (min)
Fractal	Growth	1140	0.7	1500	30	60
	Etch	1140	0	1500	10–40	60–30
Anisotropic	Growth	1140	0.7	1500	30	60
	Etch	1140	0	1500	40–100	30–10

Table S3. Conditions for size-engineering of graphene flakes.

Stage	Temperature (°C)	CH_4 (sccm)	Ar (sccm)	H_2 (sccm)	Time (min)	Size (μm)
Growth	1140	0.7	1500	30	40	~500
Etch	1140	0	1500	20	120	~2
	1140	0	1500	20	150	~1
	1140	0	1500	20	180	~0.5

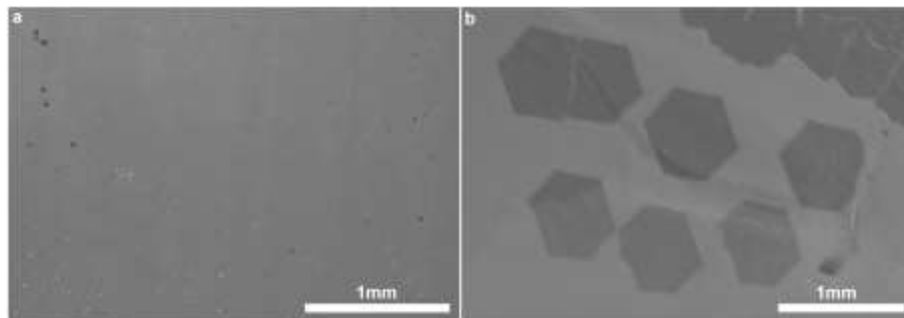

Figure S1. SEM images of large scale uniform graphene monolayer film (a) and millimeter-scale graphene single crystals (b) under the growth condition listed in Table S1.

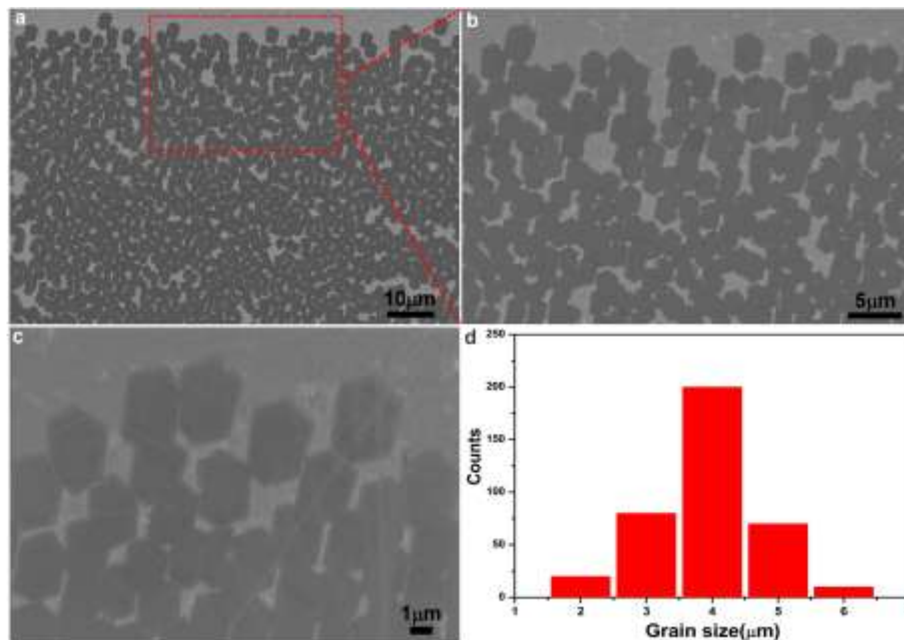

Figure S2. (a-c) SEM images of etched hexagonal graphene flakes. (d) Size statistics of graphene flakes shown in a.

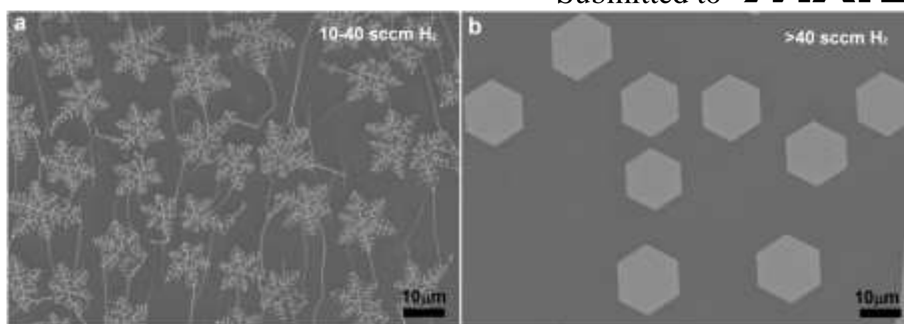

Figure S3**.** Change of graphene etching mode. (a) SEM images of fractal etching images at low H_2 flow rate. (b) Anisotropic etching images at high H_2 flow rate.

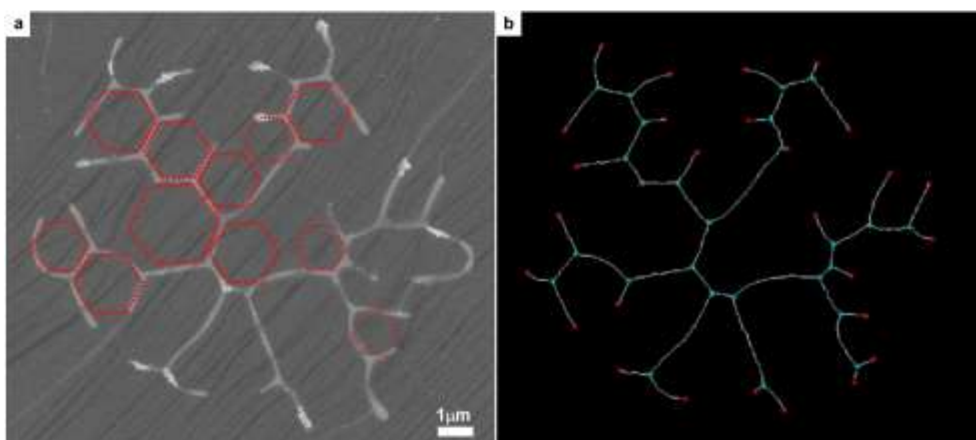

Figure S4**.** Typical hexagonal shaped graphene islands during the fractal mode etching process.

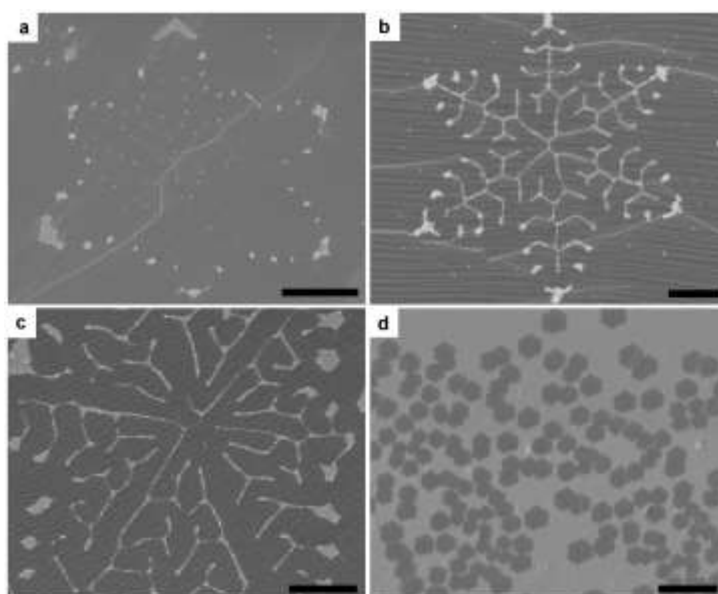

Figure S5**.** SEM images of evolutionary graphene flakes as a function of etching time. The etching time was (a) 30 min, (b) 60 min, (c) 90 min and (d) 120 min, respectively. All the scale bars are 5 μm.

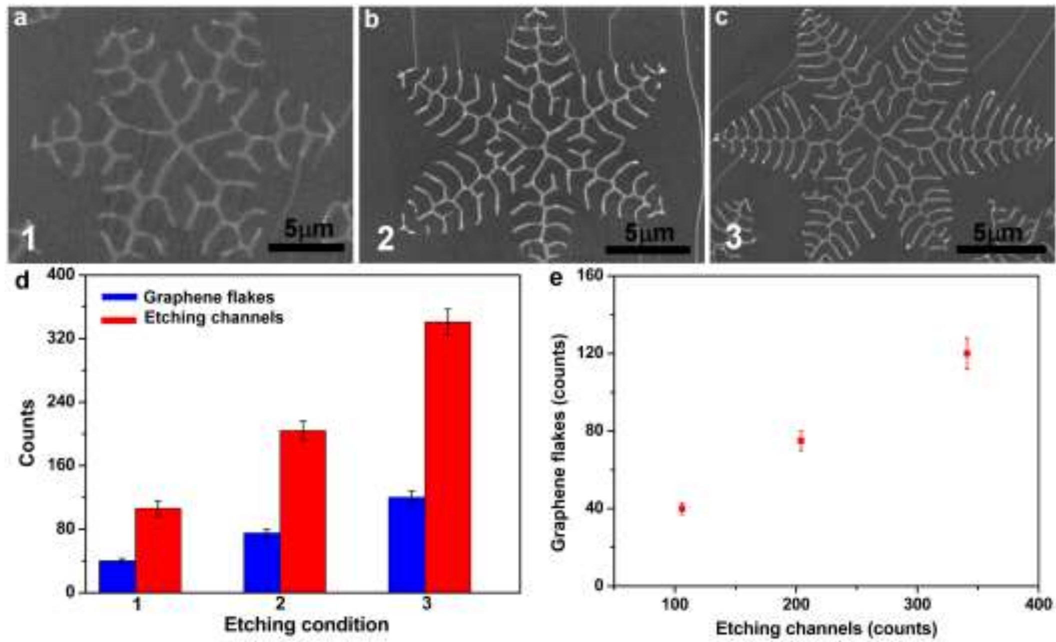

Figure S6. (a-c) SEM images of fractal graphene patterns at different etching conditions, while the etching time was 40, 60, and 80 min, respectively. (d, e) Statistics of etching channels and as-etched graphene flakes under the three etching conditions corresponding to (a-c), suggesting that the higher density of etching channels leads to the more graphene flakes.

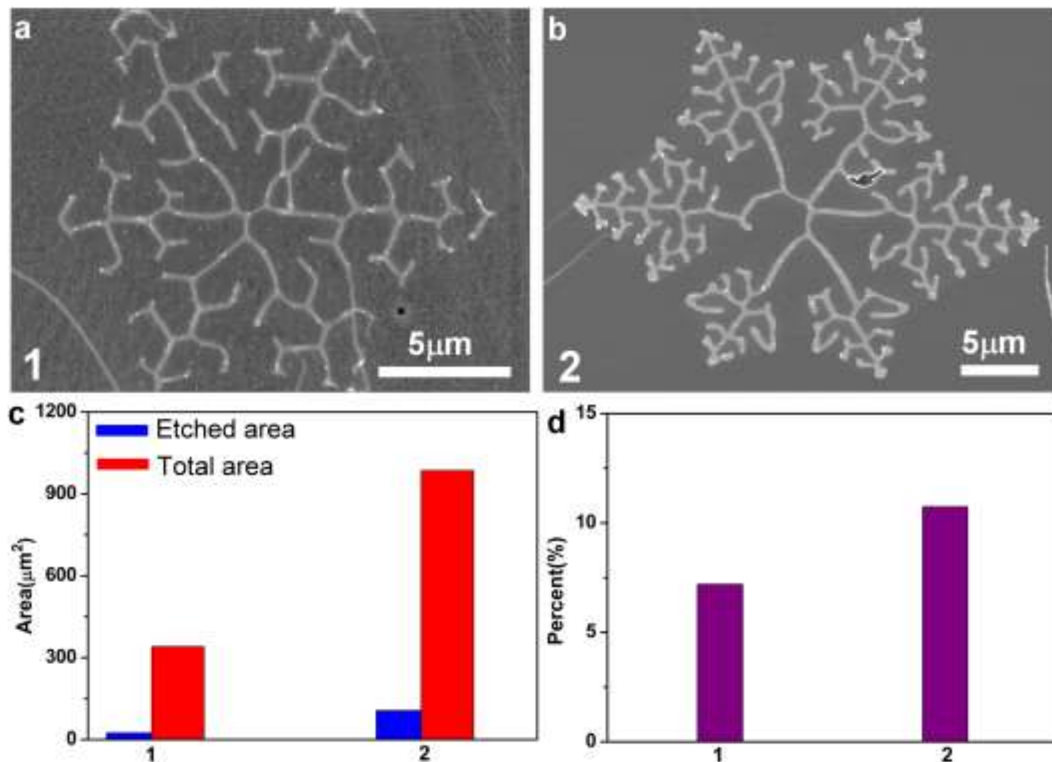

Figure S7. (a, b) SEM images of fractal graphene patterns etched from graphene film, while the etching time was 50 and 70 min, respectively. Note that the width of etching channels increases as the conditions change from 1 to 2. (c) Statistics on the etched area and total area corresponding to (a) and (b). (d) Percent ratio between etched area and total area, indicating

that the increase in the width of etching channels leads to decrease in the size of graphene flakes.

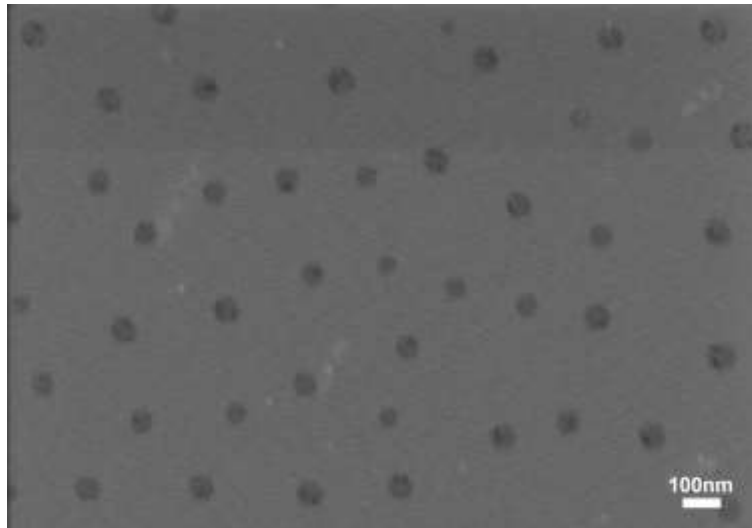

***Figure S8*.** SEM images of as-etched graphene arrays with single size at about 100 nm. The etching condition is set at 20 sccm H_2, 1500 sccm Ar for 300 min.