Electronic Supplementary Information for

Catalyst-free growth of nanocrystalline graphene/graphite patterns from photoresist

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METHODS

In-situ growth of nanocrystalline few-layer graphene (or graphite) film. The photoresist of RZJ-304 is from Suzhou Ruihong Electronic Chemical Co. LTD, and S-1813 is from Shipley. Before using, the as-received photoresist is diluted with propylene glycol monomethyl ether acetate (PMA) (99%, from Aladdin Chemistry Co. Ltd) to special concentration and spin-coated on substrates. The substrates can be SiO_2/Si, Si, Cu, ceramic (Al_2O_3), and so on. For photoresist with the thickness of 10 nm, it needs to be diluted to 1/100 (photoresist/PMA) and spin-coated on the substrates at 7000 rpm for 1 min. The thickness of the photoresist is measured by a Bruker Dektak 150 stylus profiler system with the repeatability better than 5 angstroms. The photoresist-coated substrates are then baked at 110 ^{o}C for 2 min. In the following, they are taken into a quartz tube maintained at a temperature of 1000 ^{o}C and annealed for 15 min in vacuum under the protection of 100 SCCM 5% H_2/Ar gas flow. After cooling down to room temperature, the products are brought out and characterized.

Chemical vapor deposition (CVD) growth of nanocrystalline few-layer graphene film. For the few-layer nanographene that is grown by the CVD way instead of in-situ annealing as what discussed in the paper, it is produced as following. Photoresist is firstly spin-coated on the substrates and baked at 110 ^{o}C for 2 min. And then they are partially removed by photolithography. Oxygen plasma is also used to completely clean the possible photoresist residue. Then the prepared substrates are taken into the quartz tube and heated at a temperature of 1000 ^{o}C for 15 min in vacuum under the protection of 100 SCCM 5% H_2/Ar gas flow. Few-layer graphene of around 1.5 nm is formed on the cleaned part of the substrates near the photoresist within 1 cm.

Fabrication of graphene/graphite integrated electronic device. As shown in Fig. 3a in the paper, 1.8 μm-thick photoresist patterns were firstly designed on the SiO_2/Si substrates (the first step in Fig. 3a). Then the prepared substrates are taken into the quartz tube and heated at a temperature of 1000 ^{o}C for 15 minutes in vacuum under the protection of 100 SCCM 5% H_2/Ar gas flow. After this step, the photoresist patterns are changed into graphite patterns with few-layer graphene formed around on almost the whole substrate. In order to clean the part of graphene beside source and drain, we used photolithography alignment to pattern photoresist to shield the part between source and drain, and oxygen plasma to etch the exposed part (the third and forth steps in Fig. 3a). After the photoresist shield removal (the forth step in Fig. 3a), we got integrated graphene/graphite patterns as we want for electronics.

TEM samples preparation. The TEM samples are derived from Cu substrates, which are prepared by the reported transferring procedure.[1] Marble's reagent ($CuSO_4$: HCl : H_2O :: 10 g : 50 ml : 50 ml) is used as the etchant. Poly(methyl methacrylate) (PMMA) is firstly spin-coated on few-layer graphene grown on Cu substrates and then baked at 180 ^{o}C for 2 min. In the following, they are etched by the Marble's reagent to remove the Cu substrates and then rinsed by deionized (DI) water to form PMMA/graphene films. The PMMA/graphene films are then transferred onto Cu grids and rinsed by acetone to remove the PMMA. After drying, few-layer graphene film adhering on Cu grids is ready for TEM analysis.

Samples characterization. The surface profile of the as-obtained products was measured with a Nanofirst 3600A AFM. X-ray photoelectron spectroscopy (XPS) was performed with a VG Scientific ESCALab220i-XL electron spectrometer. Raman spectroscopy was carried out on the as-produced products with a Horiba Jobin Yvon LabRAM HR Raman system using 514-nm laser excitation at room temperature. The TEM images were taken by a Tecnai F20 field-emission transmission electron microscope. The electronic properties were measured with a Keithley 4200 SCS semiconductor parameter analyzer at room temperature in air.

FIGURES AND FIGURE CAPTIONS

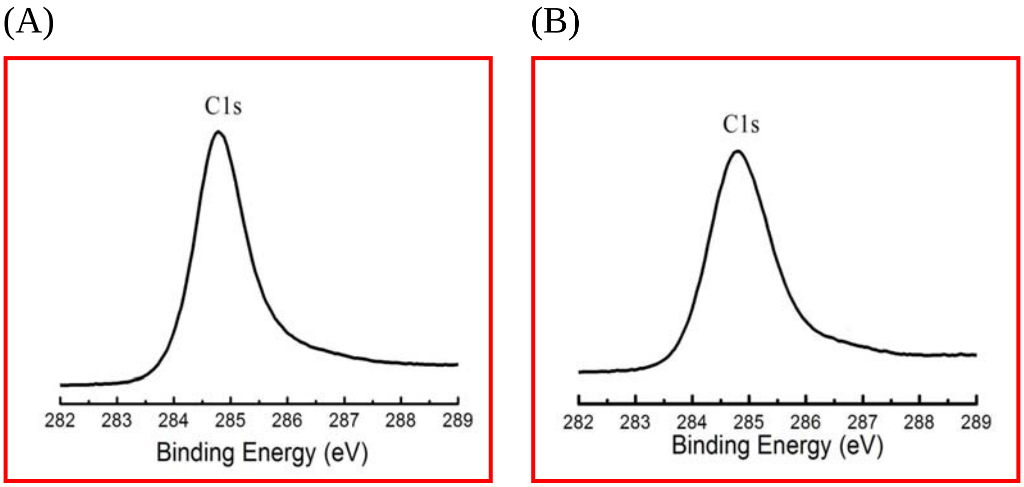

Fig. S1 X-ray photoelectron spectroscopy (XPS) results of the as-produced samples grown on SiO_2/Si and Cu substrates, respectively. (A) C1s peak of the few-layer nanographene grown on SiO_2/Si substrate. (B) C1s peak of the few-layer nanographene grown on Cu substrate. The results indicate that they are similar with a intensity at 284.8 eV, which is the typical feature of graphite-like sp^2 carbon .[1-3]

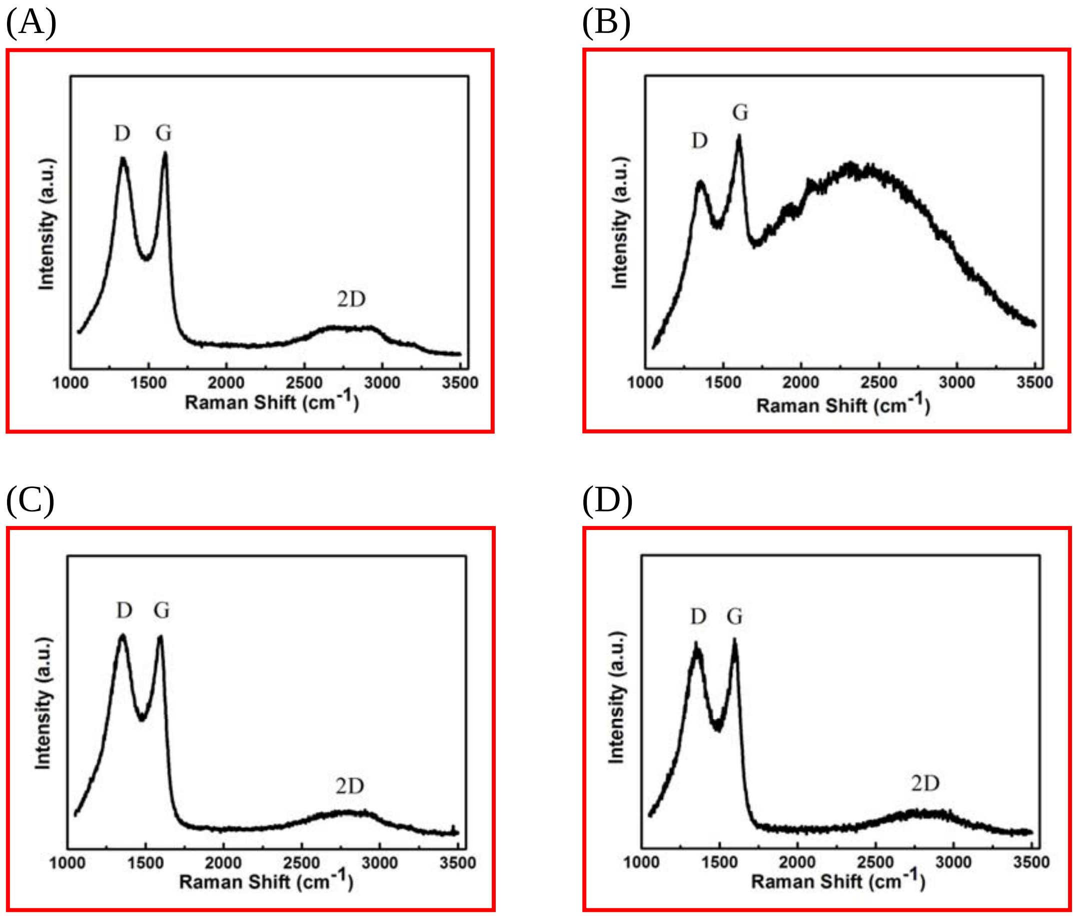

Fig. S2 Raman spectra of the few-layer nanographene grown on different substrates, which are measured with a laser of 514 nm excitation. (A) SiO_2/Si substrate, (B) Cu substrate, (C) ceramic (Al_2O_3) substrate, and (D) SiO_2/Si substrate. The sample for Fig. S2d is grown with the CVD way instead of in-situ annealing as what is discussed in the paper. In Fig. S2b, the strong background is due to the excited photoluminescence from oxidized copper. The Raman spectra indicate that they are of similar feature with a G band at around 1600 cm^{-1}, a strong D band at around 1350 cm^{-1}, and a broad 2D band, exhibiting that the products on different substrates should have similar structure. The D band is due to the defects and edge effect in the samples, which is often found in nanographene[4, 5] or reduced graphene oxide[3, 6]. With the size decreasing, the D band starts to appear due to the edge effect.[7] And it becomes strong while the size decreases to nanoscale.[8, 9] Combing with the TEM and AFM results, we can conclude that the products are mainly composed of nanographenes.

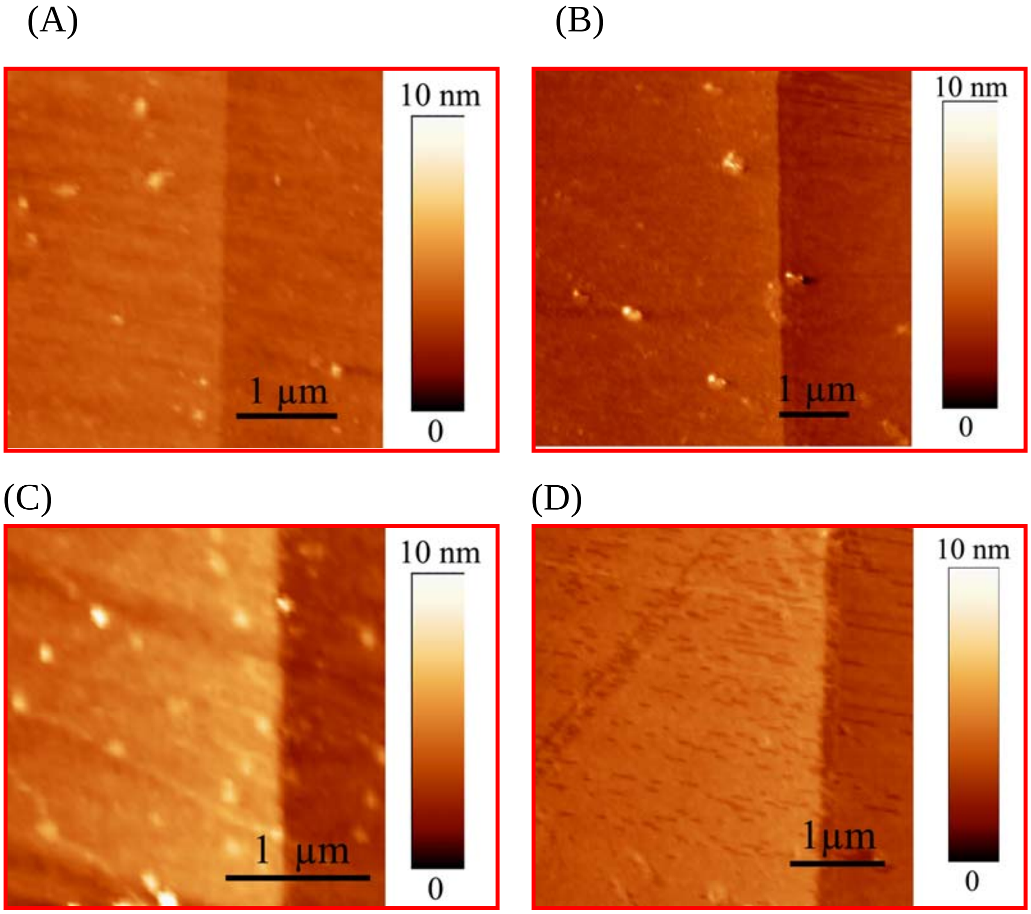

Fig. S3 AFM images of few-layer nanographene grown from photoresist with different thickness on SiO_2/Si substrates. (A) AFM image of the few-layer nanographene with the thickness of 1 nm that is from the photoresist of around 10 nm, which is the same image as Fig. 1c in the paper. (B) AFM image of the few-layer graphene with the thickness of 1.7 nm that is from the photoresist of 16 nm. (C) AFM image of the few-layer graphene with the thickness of 3 nm that is from the photoresist of 35 nm. (D) AFM image of the few-layer graphene with the thickness of 1.5 nm, which is obtained on SiO_2/Si substrate near the photoresist of 1.8 µm by the CVD way instead of in-situ annealing as what is discussed in the paper.

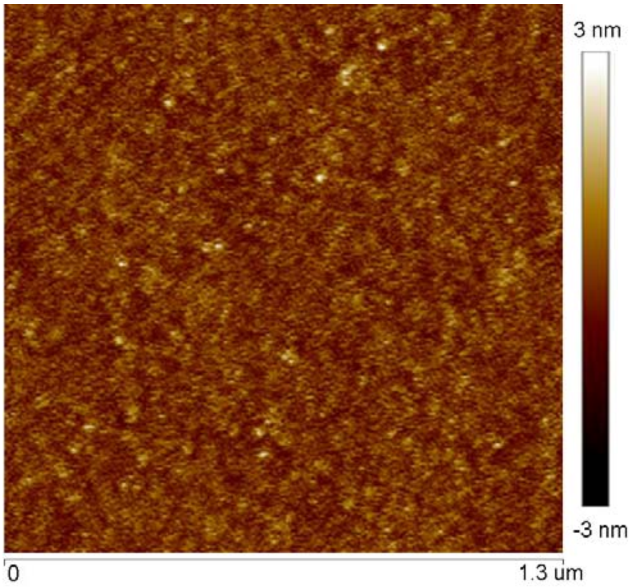

Fig. S4. AFM image of the surface of few-layer graphene. The result exhibits that the homogeneity of the film thickness is pretty good with a surface roughness around 0.5 nm.

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