Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Effects of Surface Oxidation of Cu Substrates on the Growth Kinetics of Graphene by Chemical Vapor Deposition

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In order to verify the role of Cu oxide in the nucleation stage of graphene in the OCVD process, hydrogen is flowed into the reactor for two hours after the formation of Cu surface oxide on the growth substrates. Subsequent graphene growth is under the same conditions as the regular CVD process. The thermal history of the whole process is shown in Fig. S1(a).

Because hydrogen can effectively reduce the as-grown surface copper oxide, the substrate resumes to pure Cu without surface passivation. The growth is then the same as the regular CVD process (Fig. S1(b)). The nucleation density of graphene in this process (~5×10^3 mm^{-2} as shown in Fig. S1(c)) is similar to that in the regular CVD graphene growth.

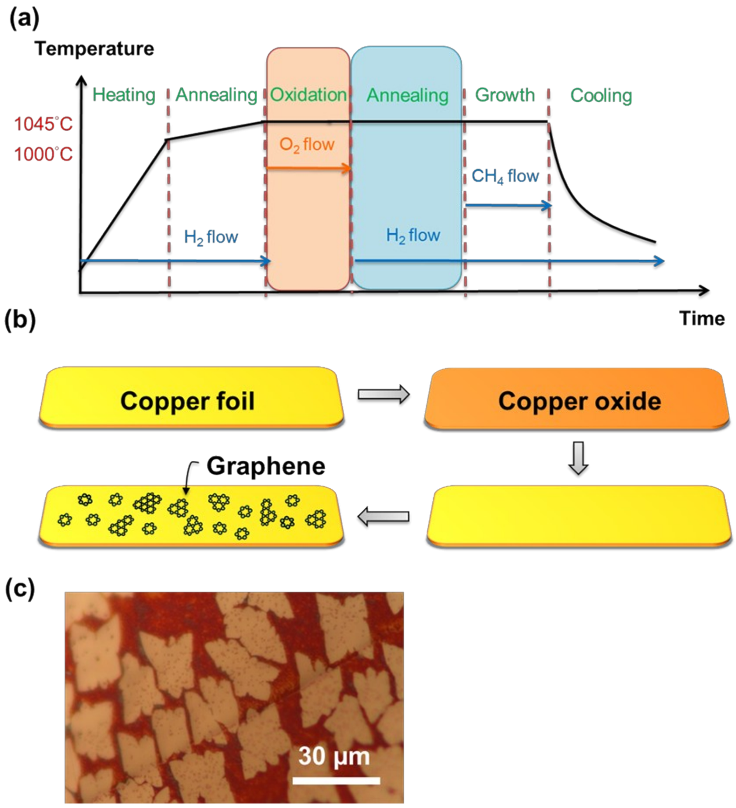

Figure S1. (a) Plot of annealing parameters in the process to verify the role of oxygen in the OCVD process. (b) Schematic illustration of the recovery of an oxidized Cu substrate for the regular CVD growth. (c) Optical microscopy image of the final graphene growth.

The electrochemical-polishing pretreatment removes the surface defects on Cu substrates. In the process, a mixture of 50 mL orthophosphoric acid (80%) and 0.08 g poly(ethylene glycol) is used as the electrolyte, and a Pt plate is used as the counter electrode. During the electrochemical polishing process, the working electrode, Cu foil, is maintained at 1.3 V for 20 min. Figures S2(a) and S2(b) are the atomic force microscopy (AFM) images of the surfaces of the Cu foils without and with the electrochemical polishing pretreatments. The surface roughness in Fig. S2(a) is 69 nm, and that in Fig. S1(b) is 7 nm.

The electrochemically-polished Cu substrates are used for the OCVD graphene growth. The resulted surface coverage of graphene on the Cu substrate is higher than the OCVD growth without the electrochemical-polishing pretreatment, e.g. 68% vs. 51% after 60 minute growth and 89% vs. 80% after 90 minute growth.

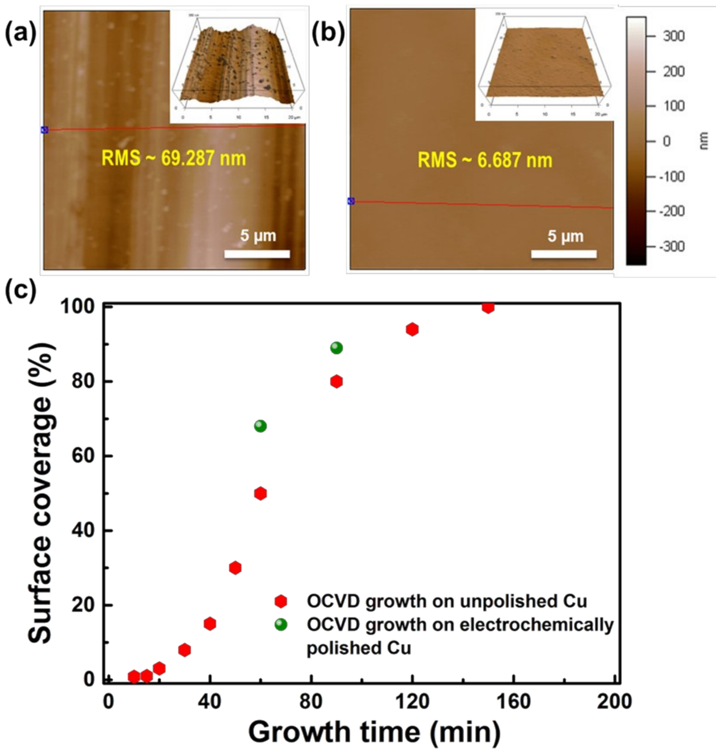

Figure S2. (a-b) Atomic force microscopy (AFM) images of the surfaces of Cu foils with only acetic etching and with electrochemical polishing. (c) Comparison of the surface coverage of graphene on the substrate of (a) and (b) in the OCVD process.

By suitably choosing the growth conditions for the regular CVD or OCVD process, we can grow graphene sheets with various domain sizes ranging from 10 μm to 1 mm. Figure S3 shows the graphene domains before they coalesce into a continuous graphene sheet at the growth conditions listed in Table S1. The sizes of graphene domains in Fig. S3(a) to S3(d) are 10 μm, 50 μm, 200 μm, and 1 mm, respectively.

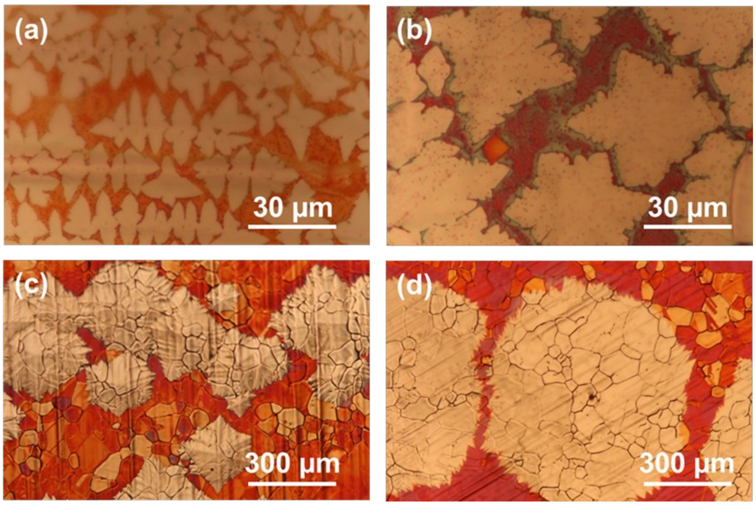

Figure S3. Optical microscopy images of graphene islands under various growth conditions. The growth conditions are listed in Table S1.

Table S1. The growth conditions for the graphene islands in Fig. S3.

Sample	Process	Position	CH_4 (mTorr)	H_2 (SCCM)	Temperature (°C)	Time (min)
S3(a)	CVD	Top surface	20	40	1045	1
S3(b)	CVD	Bottom surface	2	40	1045	8
S3(c)	OCVD	Top surface	2	40	1045	60
S3(d)	OCVD	Bottom surface	2	40	1045	120

Raman spectroscopy was used to evaluate the quality and thickness of graphene. The wavelength of the laser source was 633 nm. In the Raman spectrum of graphene, two major peaks appear at the wavenumbers of 1580 and 2700 cm^{-1}, which are referred to the G-band and 2D-band, respectively. The G-band represents the planar configuration of the sp^2-bonded carbon atoms, which constitute the graphene layer, while the 2D-band is resulted from a two-phonon lattice vibrational process. A third weaker peak known as the D-band at about 1350 cm^{-1} is due to a one-phonon lattice vibrational process. From the intensity ratio of 2D to G bands, we can determine the number of stacking graphene layers. The intensity of D-band is directly proportional to the defect density in the graphene sheet. The Raman analysis in Fig. S4 shows that the four graphene specimens used in the electrical measurements in Fig. 4 are monolayer.

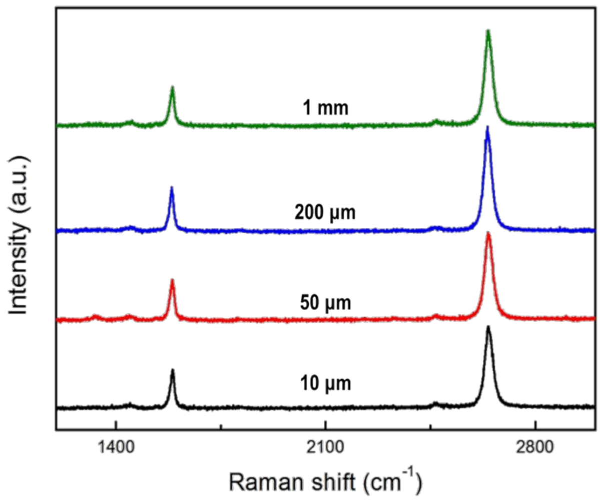

Figure S4. The Raman spectra of the graphene sheets used for the electrical measurements in Fig. 4.