Self-limiting growth of single- and double-layer graphene from ethanol

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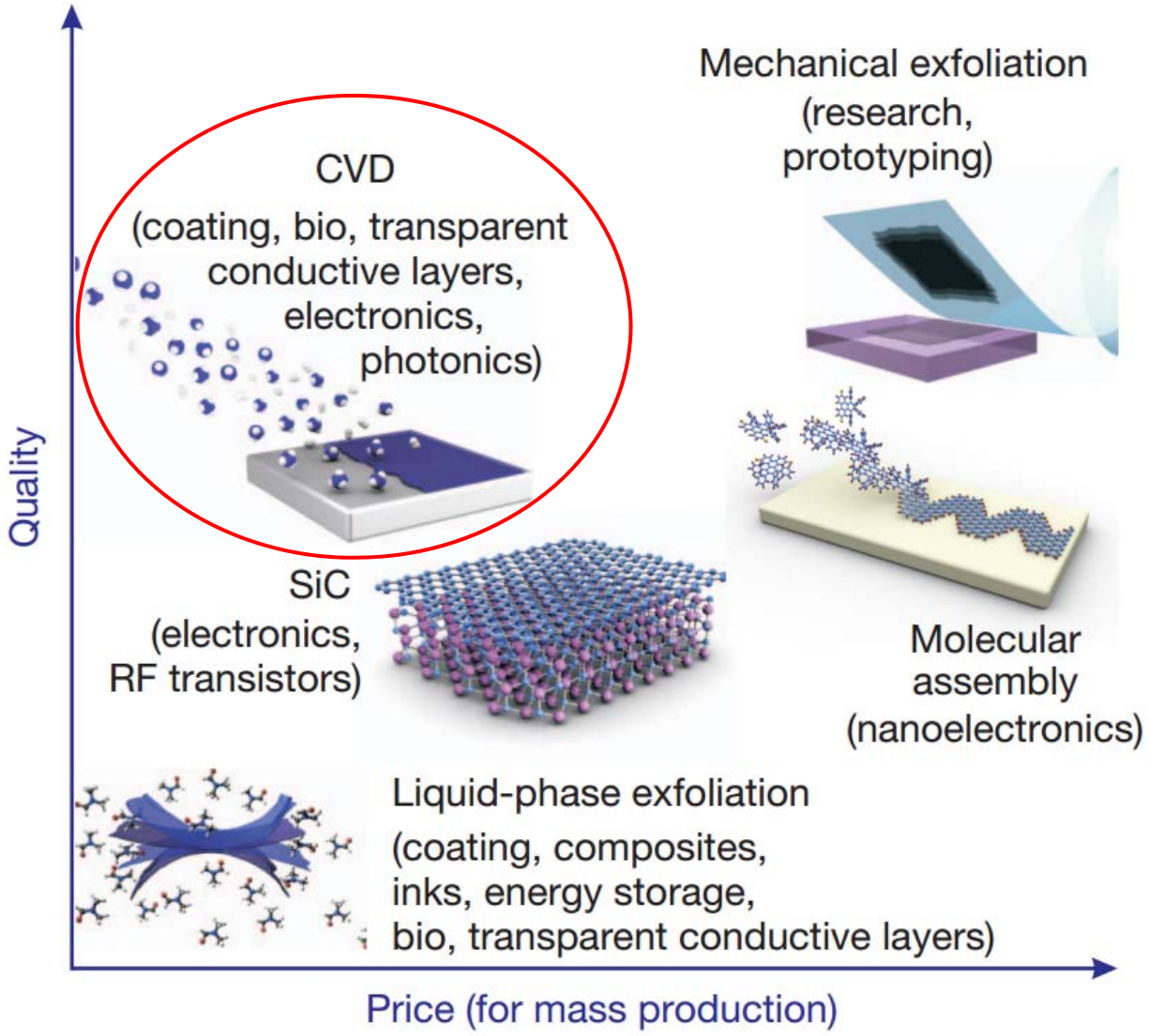
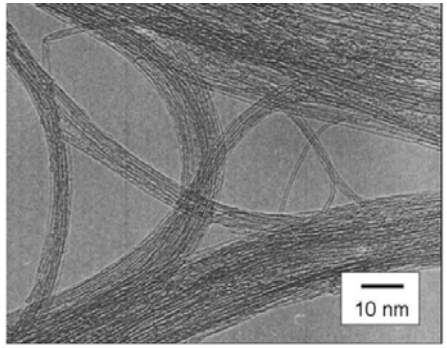
Overview of graphene synthesis

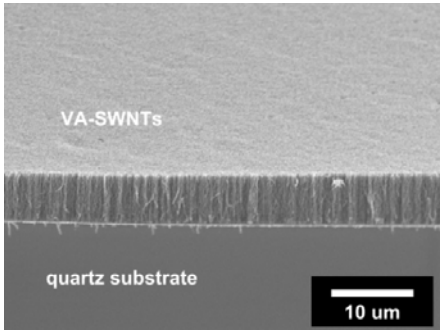


K. S. Novoselov, *et al*. *Nature* **2012**, *490*, 192.

Why Ethanol?



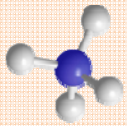
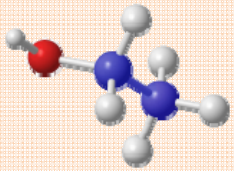
S. Maruyama, *et al*. *Chem. Phys. Lett.* **2002**, *360*, 229.



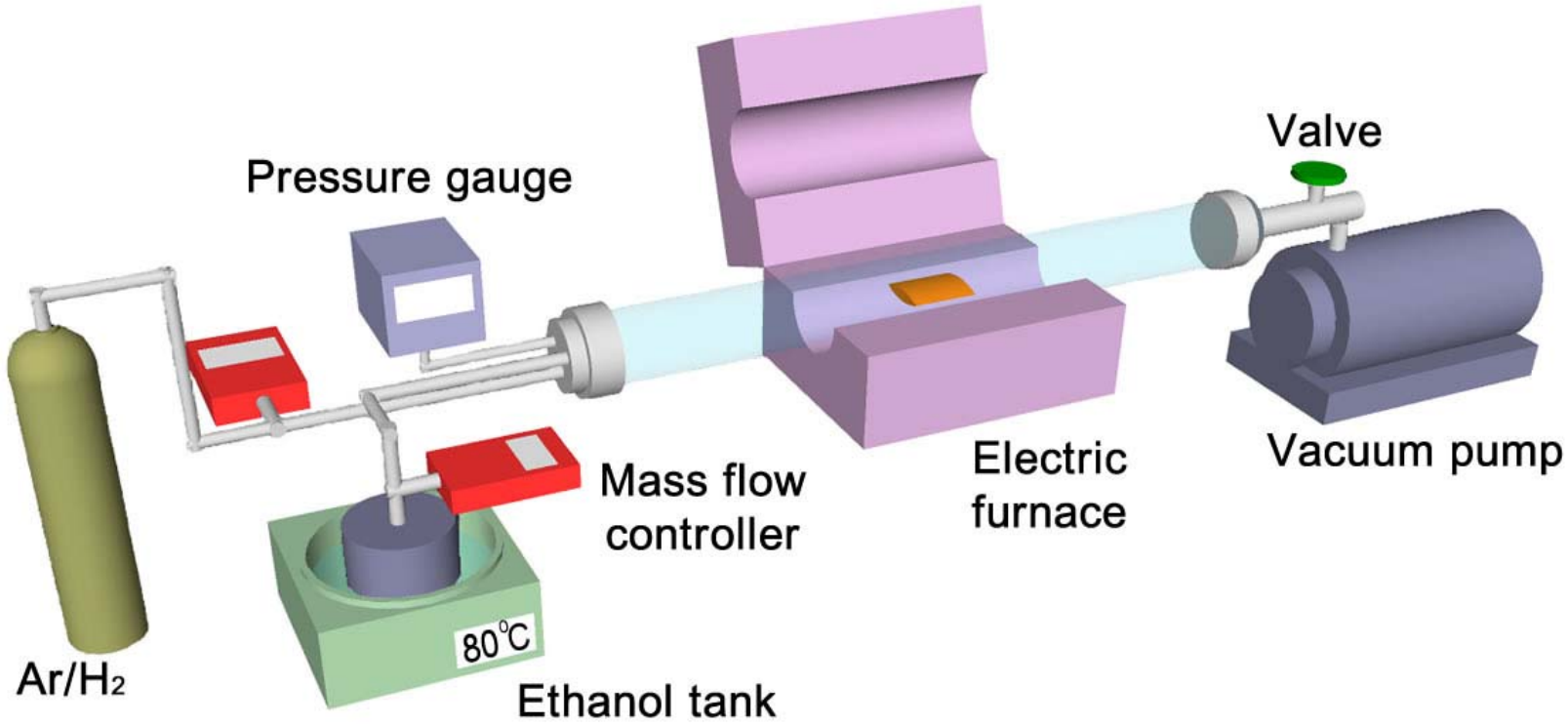
Y. Murakami, *et al*. *Chem. Phys. Lett.* **2004**, *385*, 298.

High-quality, safe, clean cheap synthesis of SWNTs

Methane and ethanol

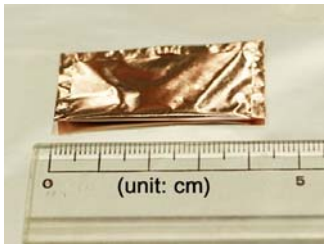
	CH_4	CH_3CH_2OH
3-D structure		
Decomposition	difficult	easy
Decomposition product	N/A	C_2H_4, CH_4, CO, H_2, H_2O, C_2H_2
Chemical reactivity	low	high

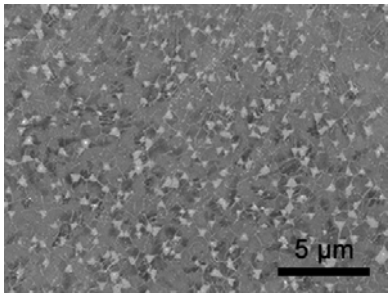
Alcohol catalytic CVD system

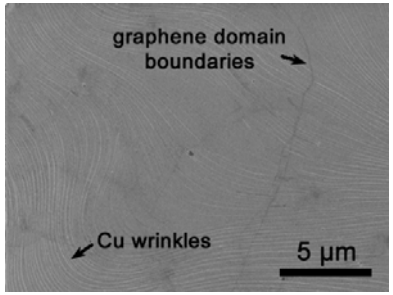


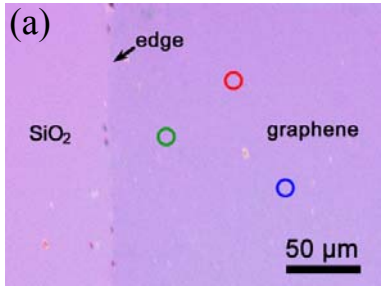
Self-limiting growth of single-layer graphene

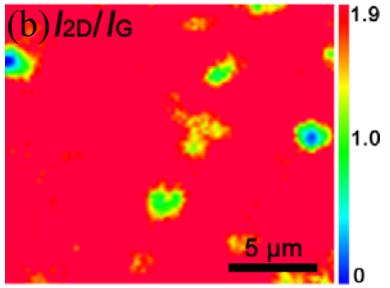
Electroplated Cu foil into an enclosure, 1000 ºC, 300 sccm Ar/H_2+10 sccm EtOH, 300 Pa, >10 min

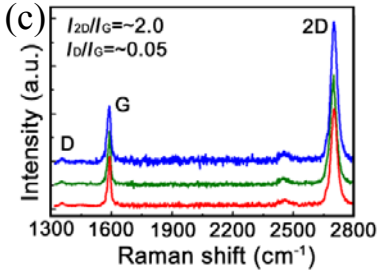


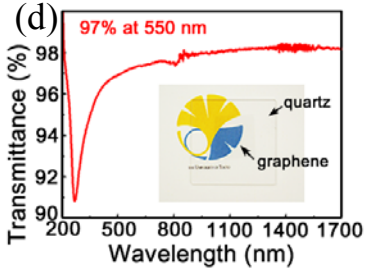












(a) Optical microscope image of transferred graphene on 300-nm-thick SiO_2;

(b) A scanning Raman map of I_{2D}/I_G;

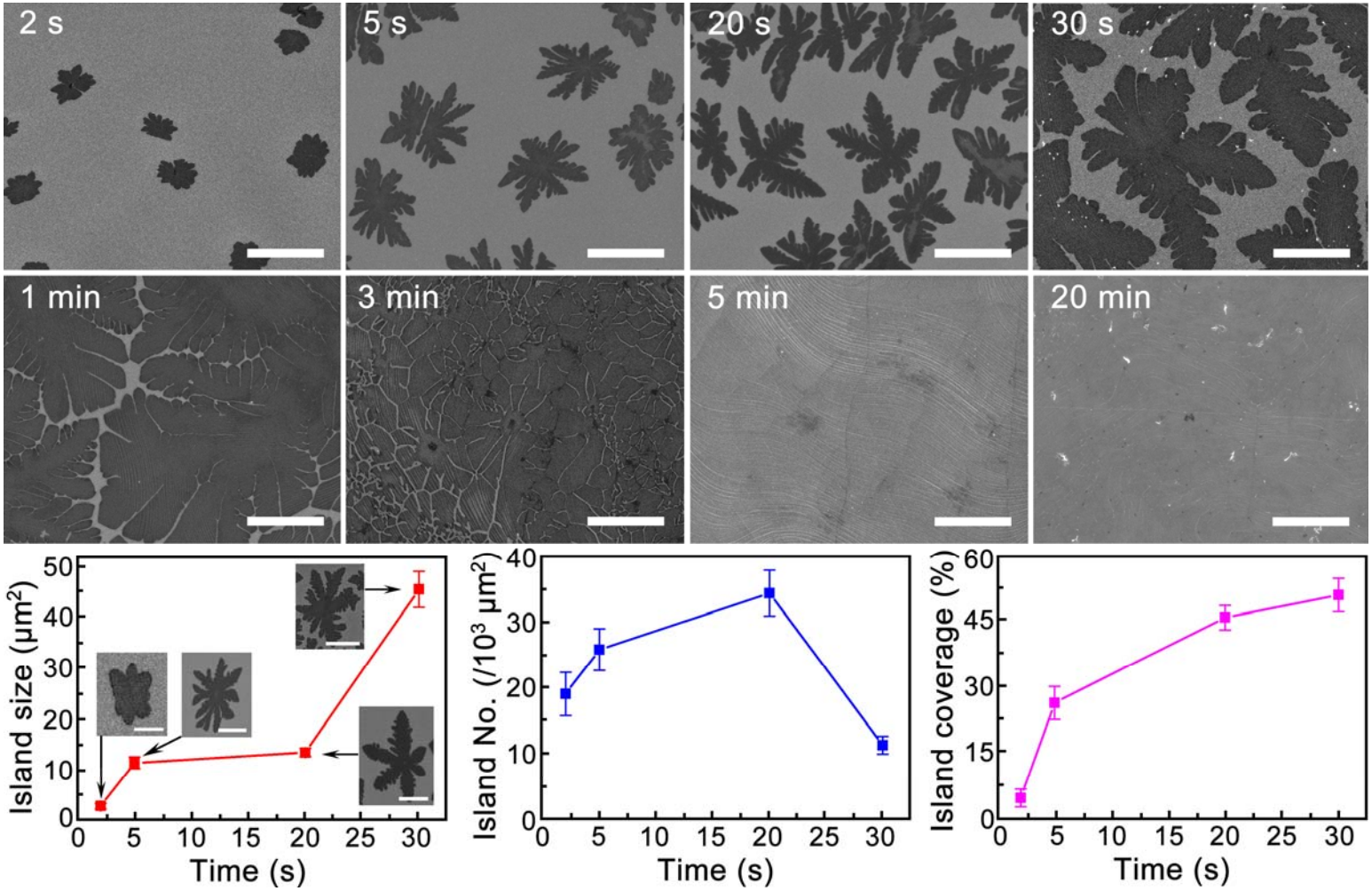
(c) Raman spectra from spots shown in (a);

(d) Transmittance of transferred graphene on quartz.

A self-limiting growth: the growth of graphene stops at SLG stage due to the lack of surface catalysis by Cu and diffusion channels for carbon atoms.

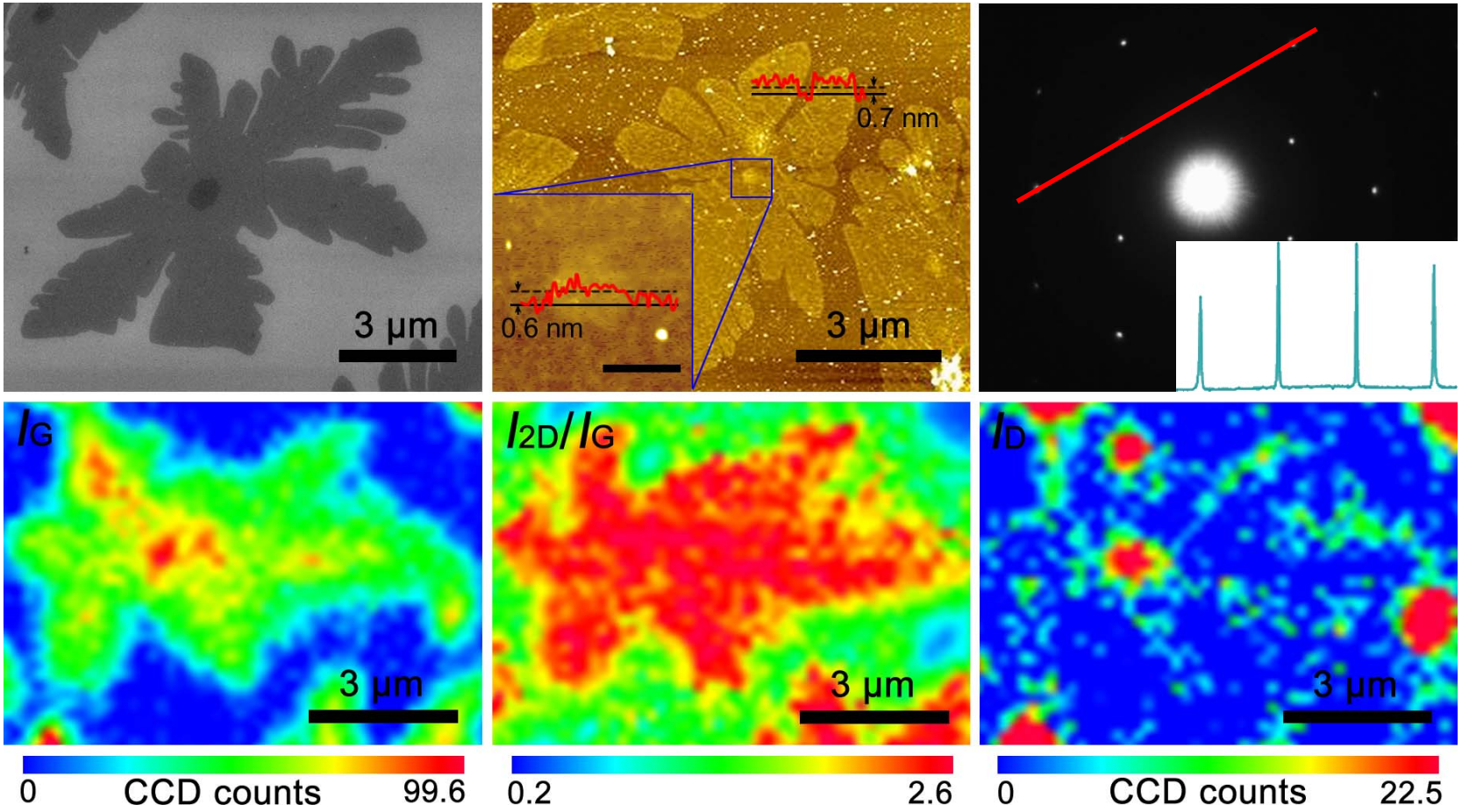
P. Zhao, S. Maruyama, *et al. J. Phys. Chem. C* **2013**, *117*, 10755.

Time-dependence of SLG growth



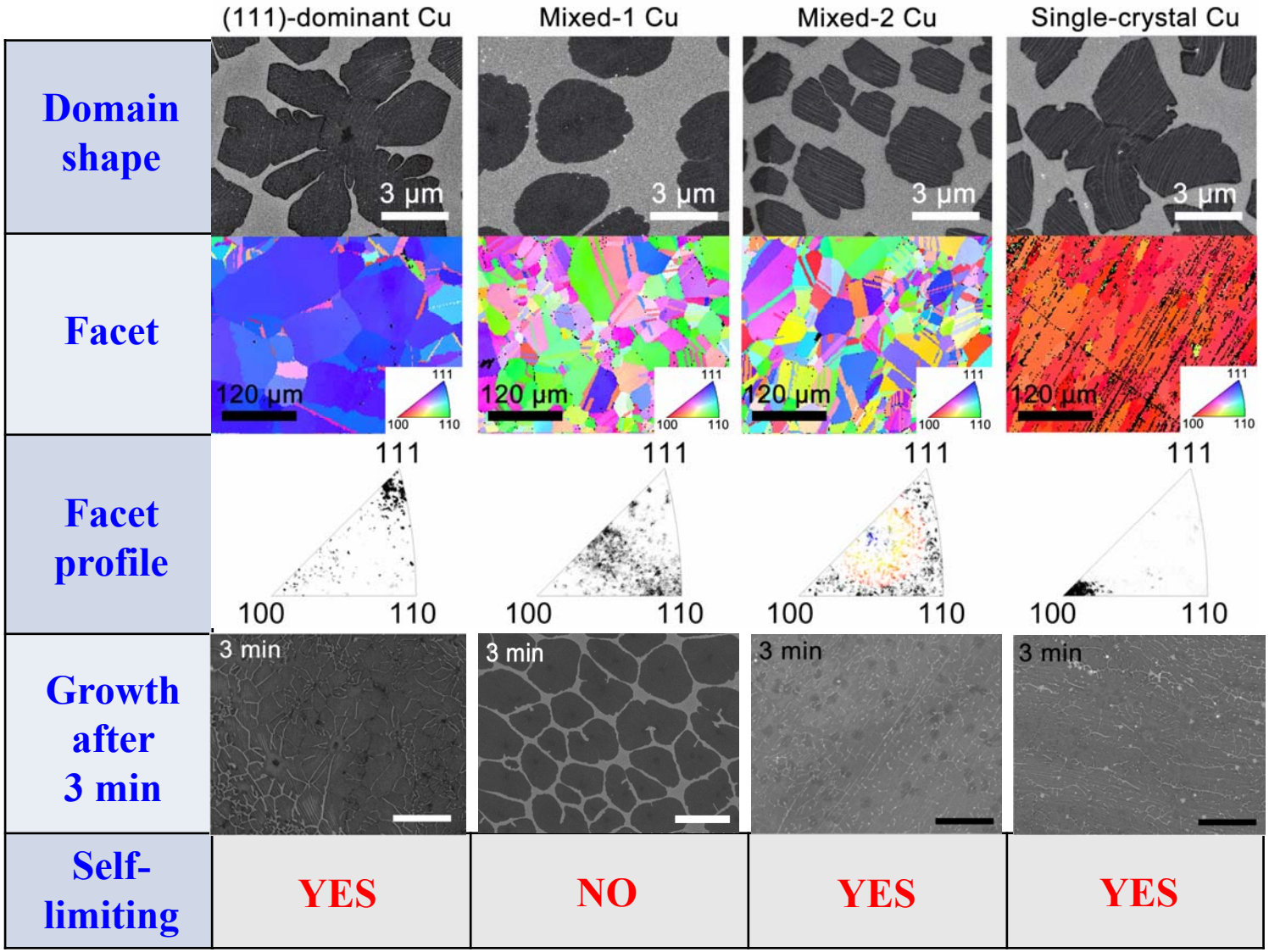
(scale bars: 5 μm)

Domain characterizations



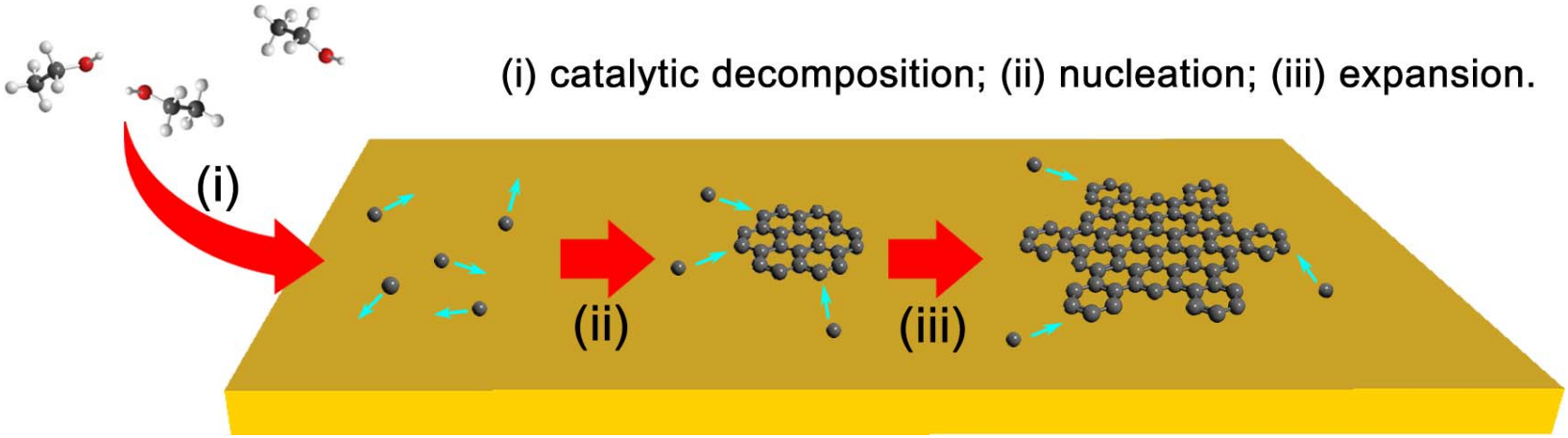
- AFM and ESBD: SLG features;
- SEM, AFM and Scanning Raman: SLG overall, and DLG nuclei at the center.

Facet-dependence of SLG growth



(scale bars: 5 μm)

Growth mechanism of SLG

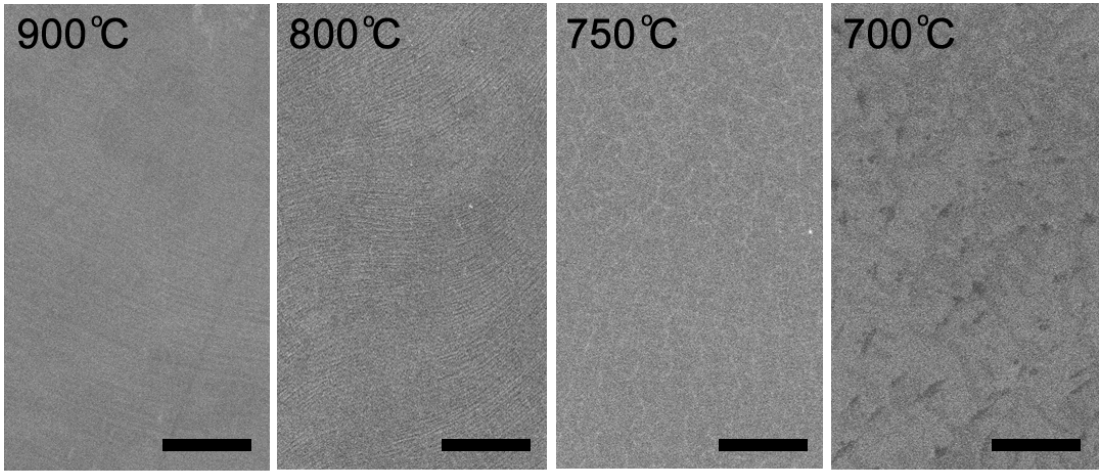


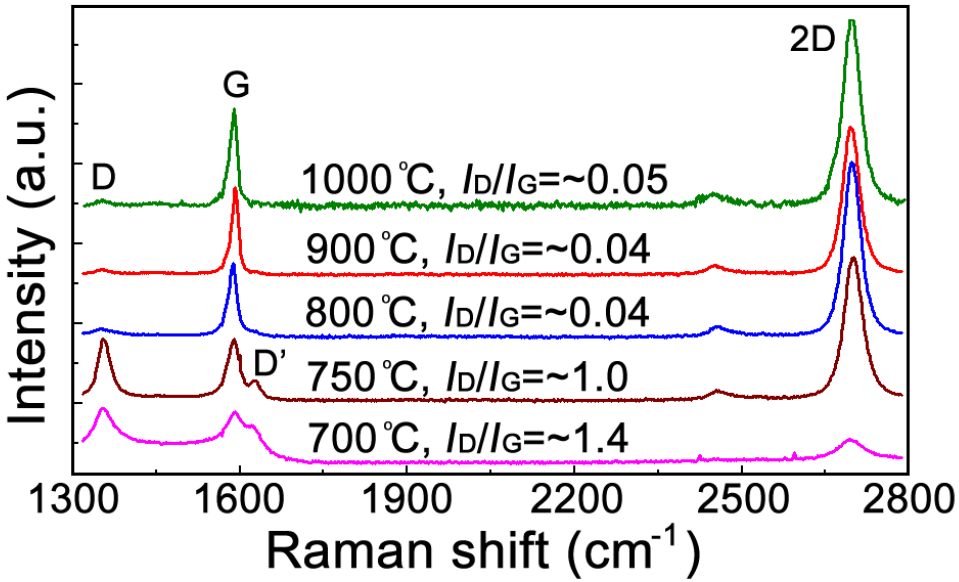
(i) At high T ethanol are catalyzed into active species by Cu and chemically adsorbed on the Cu surface.

(ii) Carbon atoms freely diffuse and aggregate on the active sites of Cu surface to reach a supersaturated state and nucleate.

(iii) Diffused carbon atoms are captured by the nucleus edges, and the nuclei are expanded into domains with dendritic shapes.

Low-temperature SLG growth



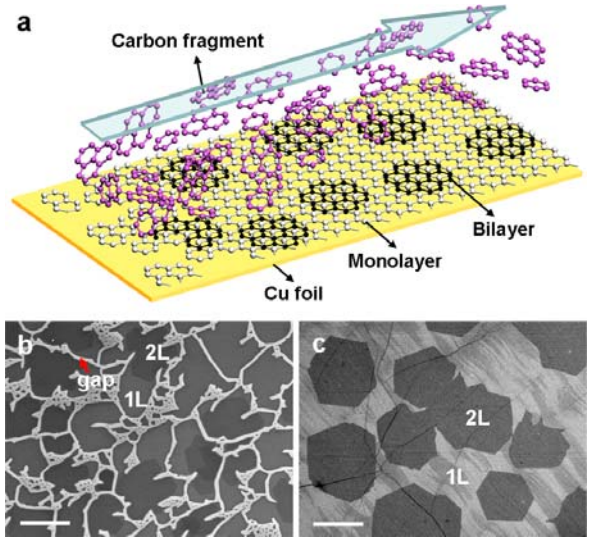


(scale bars: 5 μm)

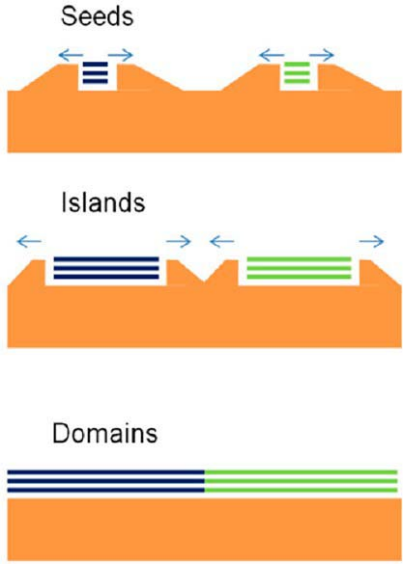
Efforts for double-layer graphene growth

Because the second layer is grown below the first, to obtain bilayer graphene growth, we need:

1. Continuous carbon supplies into the system
2. Catalysis to the carbon precursor
3. Diffusion channel for carbon species to the new layer



Liu, L.; Duan, X.; et al., *ACS Nano* **2012**, *6*, 8241



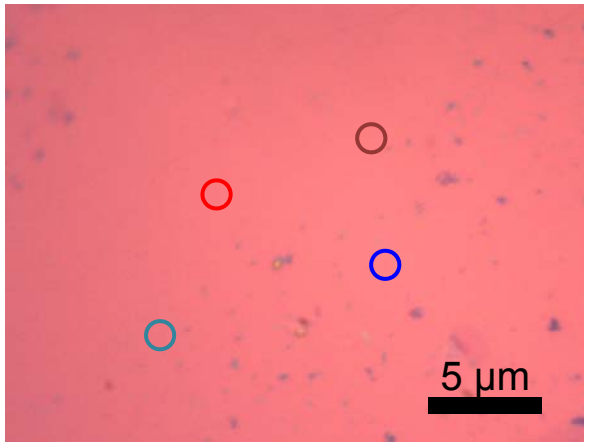
Sun, Z.; Tour, J. M.; et al., *ACS Nano* **2012**, *6*, 9790

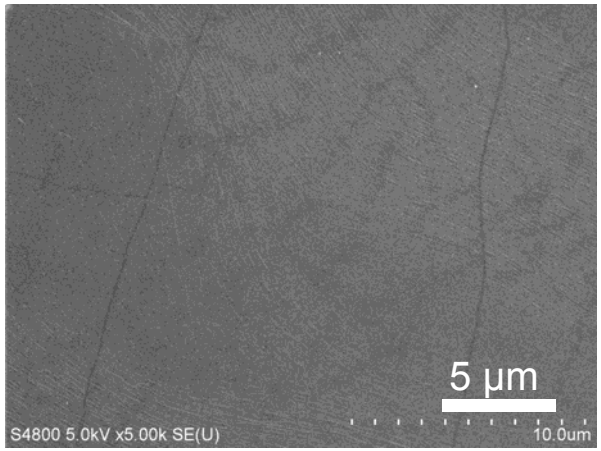
In both cases, high-purity H_2 and a high H_2/CH_4 ratio are critical.

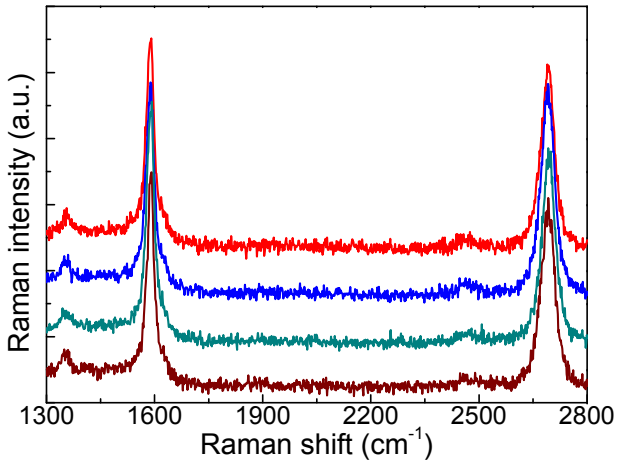
Why ethanol? ➡ **Ethanol realizes the self-limiting growth of DLG in a much simpler way.**

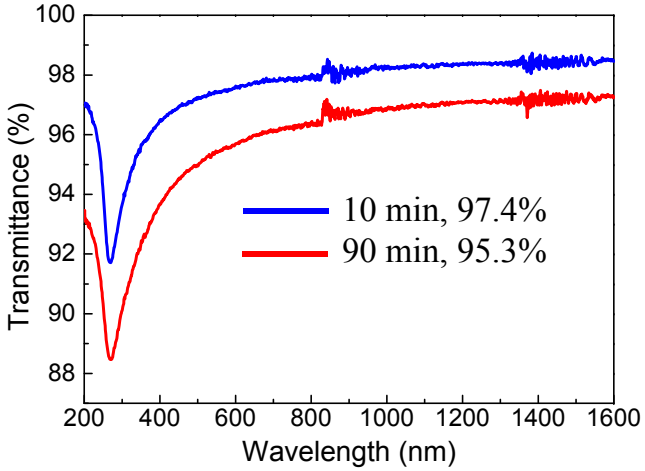
Self-limiting growth of DLG from ethanol

Electroplated Cu foil into an enclosure, 1000 ºC, 300 sccm Ar/H_2+50 sccm EtOH, 350 Pa, >90 min

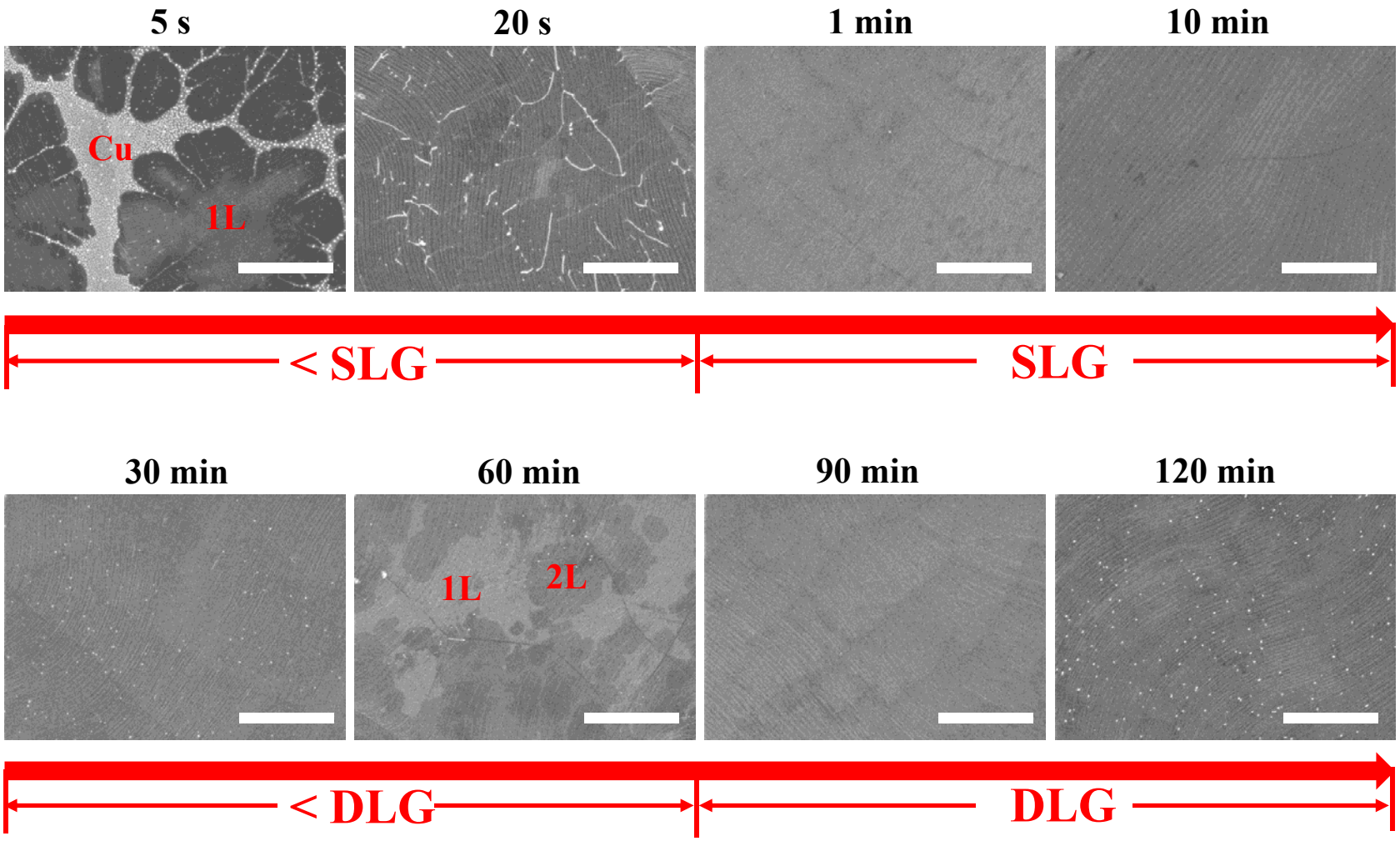






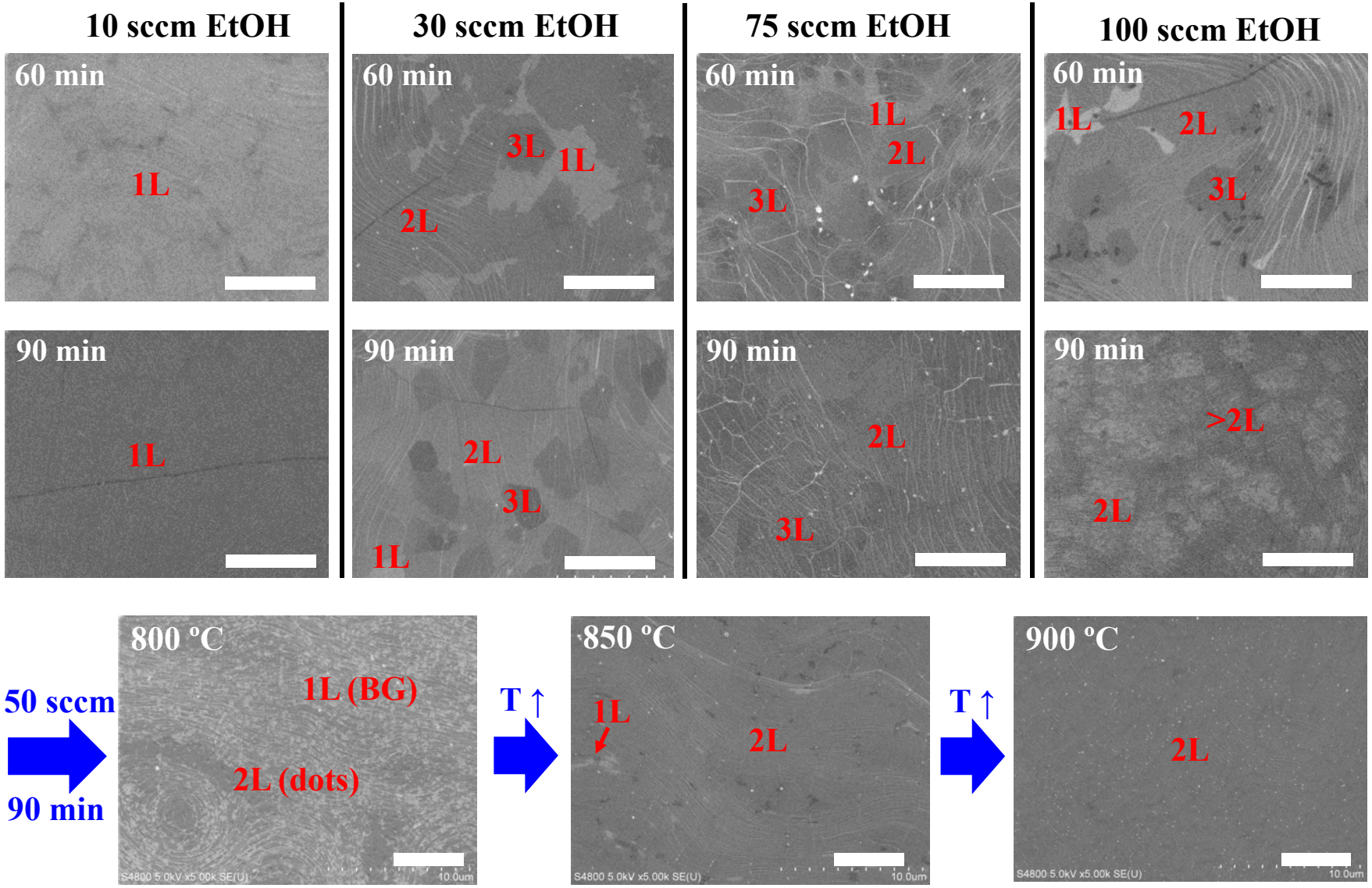


Time-dependence of DLG growth



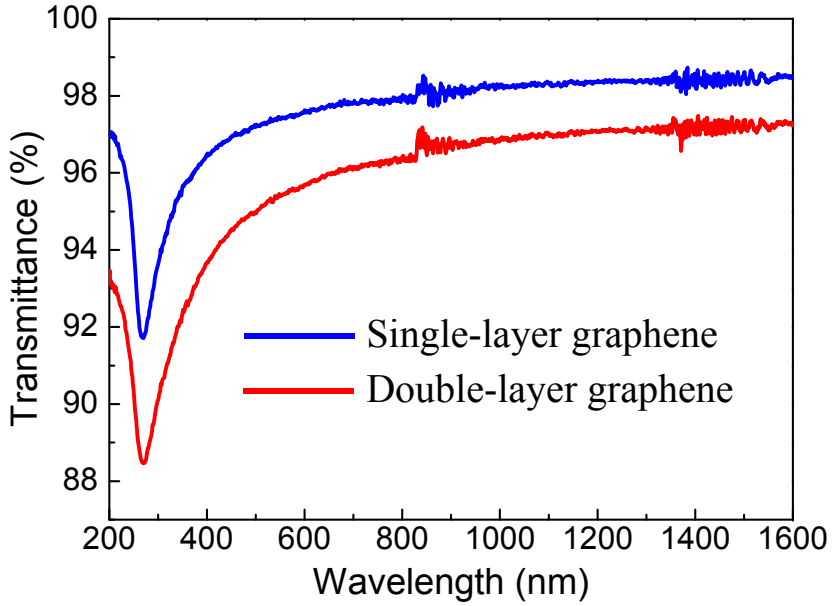
(scale bars: 5 μm)

Flow-rate and temperature dependence



(scale bars: 5 μm)

Summaries



- Ethanol can serve as an effective precursor for single- and double-layer graphene growth;
- SLG growth is a surface-mediated process and follows a self-limiting growth behavior;
- Ethanol can also break the self-limiting to initial the growth of additional layers;
- With a careful control of flow rate and temperature, self-limiting growth of DLG can be achieved, but the growth mechanism remains unknown.