The effect of residual oxygen on the production of graphene by atmospheric pressure chemical vapor deposition

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To be of use in industrial applications, large-area uniform graphene films of high structural quality must be produced at low cost. In that context, catalytic chemical vapor deposition (CVD) shows great promise to fulfill these objectives. The first demonstration of graphene growth by CVD was reported in 2009 on copper foils under low pressure [1]. In terms of simplicity and cost-effectiveness, atmospheric pressure CVD [2,3,4] is an interesting alternative to low pressure CVD since it avoids the use of vacuum systems.

In the present work, the growth of graphene by atmospheric pressure CVD on copper foils with methane is explored. The focus is put on the necessity of using hydrogen during the cooling and growth steps (in addition to extra pure argon). First, it is observed that, in the absence of hydrogen during natural (slow) cooling, graphene is not obtained. By contrast, the addition of a small amount of hydrogen or fast cooling leads to appreciable graphene coverage. X-ray photoelectron spectroscopy evidences that natural cooling without hydrogen results in heavily oxidized and amorphized graphene. A likely explanation for this observation is the seemingly inevitable presence of residual oxygen from ambient air in the growth atmosphere, which strongly damages graphene upon too long exposure at high temperatures. Likewise, graphene formation is drastically inhibited if hydrogen is not present during the growth step. The conclusion is that, in these conditions, hydrogen must be present all along the process to prevent a re-oxidation of the copper surface during growth and also to protect graphene from etching by oxygen during natural cooling. In the best conditions, micrometer-sized graphene hexagons are formed [3]. Raman spectroscopy and scanning electron microscopy confirm that these domains are monolayer, bilayer or few-layer. The monolayer hexagons are found to be of excellent structural quality, as testified by the absence of D band in the Raman spectra.

As a summary, even if the occurrence of oxygen can apparently not be avoided in simple atmospheric pressure CVD systems, its negative effects can be eluded by a careful dosing of hydrogen during the growth and cooling steps. In this way, graphene hexagonal domains of high structural quality can be synthesized.

References

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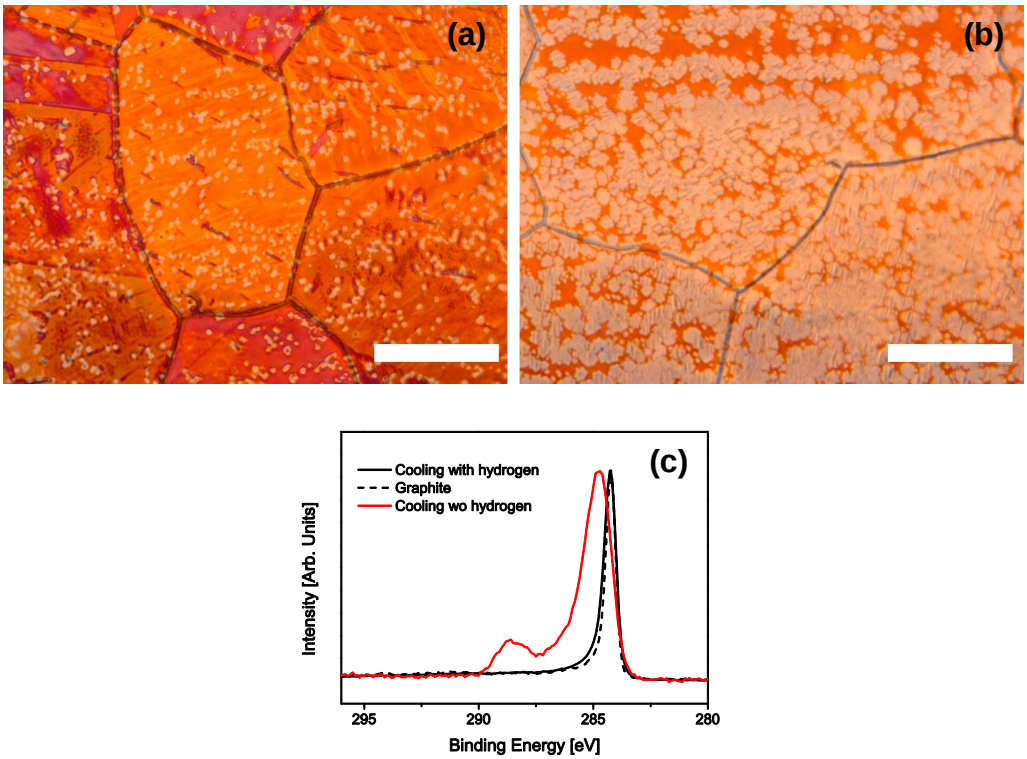

Figure 1: Optical microscopy of graphene on copper foils oxidized under air after thermal treatment on a heating plate (a) for natural cooling without hydrogen and (b) for natural cooling under hydrogen. Scale bars are 20 µm. (c) X-ray photoelectron C 1*s* spectrum of the two previous samples compared with graphite.

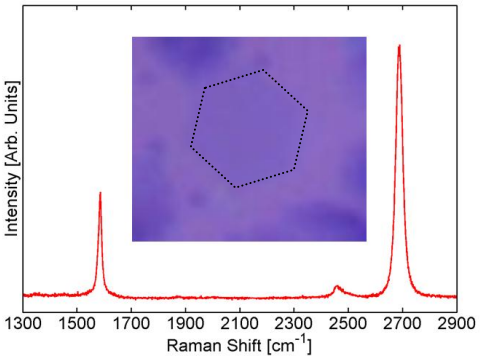

Figure 2: Raman spectrum of a typical monolayer graphene hexagon. Inset: optical microscopy image of the corresponding hexagon transferred onto 300-nm-thick SiO_2.

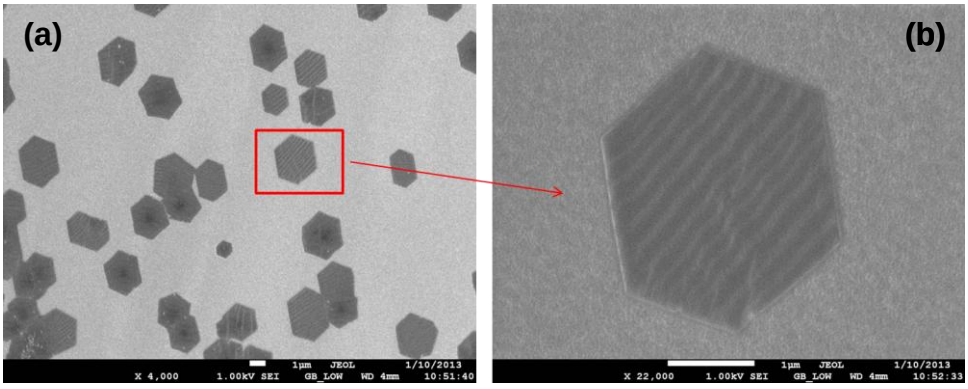

Figure 3: Scanning electron microscopy views of (a) monolayer and few-layer graphene hexagons on copper and (b) focus on a monolayer graphene hexagon.