Ultra-Clean Freestanding Graphene by Pt-metal catalysis

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Abstract

The physical and electronic properties of graphene(*1*, *2*) depend to a large extent on its defect-free structure and its cleanliness. Scattering of transport electrons at impurities is one of the major drawbacks in view of employing graphene in electronic devices(*3–5*). Furthermore, when using graphene as a substrate in electron microscopy, the presence of residues is obstructive because the latter are often of the same size as the object under study(*6*). While the growth of defect-free single-layer graphene by means of chemical vapor deposition (CVD) is nowadays a routine procedure(*7*, *8*), easily accessible and reliable techniques to transfer graphene to different substrates in a clean manner are still lacking. The common technique for the transfer of the layers grown by means of CVD on a metallic substrate (usually nickel or copper) onto an arbitrary substrate requires a polymer support layer, usually polymethyl methacrylate (PMMA), spread or spin-coated over the graphene(*5*, *9*, *10*). The subsequent removal of this approximately 100 nm thick PMMA layer is a challenge, and extensive efforts have been undertaken in the past few years to establish a reliable technique to retrieve pristine graphene without PMMA residues(*3–5*, *11–14*). Well known chemical etchants for PMMA are acetone and chloroform(*15*). Unfortunately, wet chemical treatment of the polymer leads to contaminated graphene layers with excessive residues. Thermal annealing at temperatures in the range of 300°C–400°C in vacuum(*12*, *15*) or in an Ar/H_2 atmosphere(*15*) appears to promote the cleaning process. However, besides the fact that these techniques are not easily available, they do not lead to ultra-clean freestanding graphene. We have discovered a method for preparing ultra-clean freestanding graphene using the catalytic properties of platinum metals. Complete catalytic removal of polymer residues only requires annealing in air at a temperature between 175°C and 350°C.

After the catalytic removal of the PMMA layer, the cleanliness of the freestanding graphene sheets is characterized in the low-energy electron point source microscope. In its holographic setup inspired by the original idea of Gabor(*16*), a sharp (111)-oriented tungsten tip acts as source of a divergent beam of highly coherent electrons(*17*). The electron emitter can be brought as close as 200 nm to the graphene sample with the help of a 3-axis piezo-manipulator. Part of the electron wave impinging onto the sample is elastically scattered and forms the object wave, while the un-scattered part of the wave represents the reference wave(*18*). At a distant detector, the interference pattern between the object wave and the reference wave – the hologram – is recorded. The magnification of the microscopic record is given by the ratio of detector-tip-distance to sample-tip-distance and can be as high as one million. Figure 1(a) displays a hologram of a freestanding ultra-clean graphene layer covering a 500 nm diameter hole recorded with our low-energy electron point source microscope at a kinetic electron energy of 61 eV and a total electron current of 50 nA. Clean freestanding graphene is almost transparent even for low-energy electrons(*19*, *20*) and the presence of graphene can only be confirmed by observing individual adsorbates, possibly from the gas phase, sticking to the monolayer. For comparison, figure 1(b) shows an image of freestanding graphene (70eV, 500nA), where the polymer layer was removed in the common manner by dissolving it in acetone. The resulting graphene layer is still polluted and almost opaque, even when imaged with a tenfold increased electron current, and the presence of PMMA residues is evident. Similar results to those shown in figure 1(a) were also obtained with Pd as catalyst. Attempts to use other metals, such as gold, for cleaning graphene failed. Low-energy electron microscopy investigations revealed, in these cases, either empty holes where the graphene broke, or opaque holes where the graphene was heavily contaminated. The cleanliness of the graphene sheet prepared as explained above was also verified by TEM investigations at 80 keV. Figure 1(c) shows a hole of 500 nm in diameter entirely covered by an ultra-clean single-layer graphene sheet. The presence of graphene is only detected at high magnification were the unit cell becomes apparent (Figure 1(d)). Specialists in TEM studies on graphene have confirmed that such wide areas of atomically clean freestanding graphene have never been observed before.

Here, we will describe in detail the preparation process for obtaining ultra-clean freestanding graphene by Pt-metal catalysis. The presentation of low-energy electron holography and TEM investigations will demonstrate that areas of ultra-clean freestanding graphene as large as 2 square microns can now routinely be prepared. These findings will have important impacts for the application of graphene in the field of electron microscopy and possibly in electronics.

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Figures

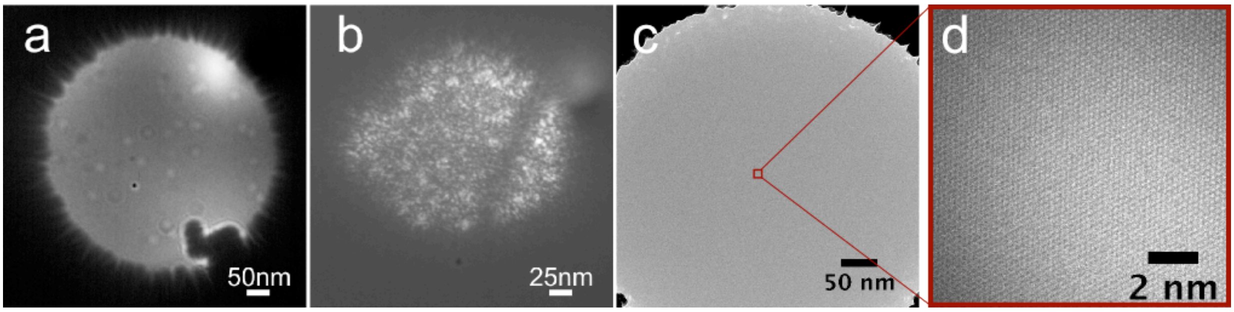

Figure 1: (a) Low-energy electron hologram of ultra-clean freestanding graphene prepared by our patented method, (b) electron transmission after the removal of the PMMA layer with acetone, (c) TEM image of a hole of 500 nm in diameter entirely covered with ultra-clean freestanding graphene, (d) high magnification image of the region marked by a red square in (c).