

Growing high-quality graphene from incredible solid materials

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The synthesis of nanocar¹, nanotruck² and nanoworm³ by Tour and co-workers demonstrates the ability of this research group to prepare exotic organic nanomaterials. The availability of buckminsterfullerene (C₆₀) co-discovered by Richard Smalley of Rice University, Texas, USA, presumably motivated Tour also working in the same university to synthesize nanocar using C₆₀ as wheels. Tour's realization of the potential applications of carbon nanomaterials, particularly in molecular electronics, led to the production of not only graphene nanoribbons on a large scale by a simple solution-based oxidative longitudinal unzipping of multiwalled carbon nanotubes⁴, but also of pristine graphene from unexpected and incredible starting materials like food, waste and insect⁵.

Graphene, an atom-thick mesh of carbon atoms arranged in a honeycomb pattern, is considered to be the mother of all graphitic materials like fullerenes, carbon nanotubes and graphite⁶. Many extraordinary attributes of graphene, like electrical, mechanical and thermal pro-

perties, high carrier mobility, ambipolar electrical field effect, tunable band gap, room temperature quantum Hall effect and high elasticity⁶ are so fascinating that the world's thinnest, strongest and stiffest material has been showered with media attention as companies vie to bring those attributes to the market. Though in 2004, Novoselov *et al.*⁷ obtained graphene by micromechanical cleavage of highly oriented pyrolytic graphite (Scotch-tape method) in small yield, the past seven years have witnessed several different methods for the production of graphene. These include epitaxial growth on electrically insulating surfaces such as SiC, chemical vapour deposition (CVD) of hydrocarbons on metal surface (see refs 6, 8, 9), liquid-phase exfoliation of graphite¹⁰, and the reduction of graphene oxide obtained from graphite oxide⁸ by a variety of reducing agents. The last mentioned protocol yields only chemically modified graphene. While Li *et al.*¹¹ reported the growth of graphene by low-pressure CVD in copper-coil enclosures employing the gaseous precursor meth-

ane in the presence of hydrogen, Sun *et al.*¹² used poly(methyl methacrylate), fluorene and sucrose as solid carbon sources to grow monolayer graphene on a Cu catalyst in an atmosphere of reductive gas (H₂/Ar). Because these precursors are purified materials, the production of monolayer graphene becomes expensive. Cheap methods for the large-scale production of high-quality graphene from less expensive precursors receive greater attraction because of a variety of possible applications of graphene in myriad areas. In this context, the method developed by Tour and his group for the growth of high-quality graphene monolayer from low value and unbelievable carbon-containing materials such as cookies and chocolates (food), grass, plastics and dog faeces (waste), and cockroaches (insects) without any purification stands unique⁵. This group has demonstrated the growth of monolayer pristine graphene from solid carbon sources atop a copper foil⁵. To obtain graphene monolayer, 10 mg of the dry carbon source was placed atop the copper foil supported in a quartz boat and annealed in a tubular furnace (Figure 1 a) at 1050°C for 15 min under low pressure H₂ and Ar. When grass and dog faeces were employed as carbon precursors for the removal of moisture, the samples were heated in a 65°C vacuum (102 torr) oven for 10 h.

As the quartz boat has a semicircular shape, the slightly bent Cu foil is supported by the quartz boat (Figure 2)

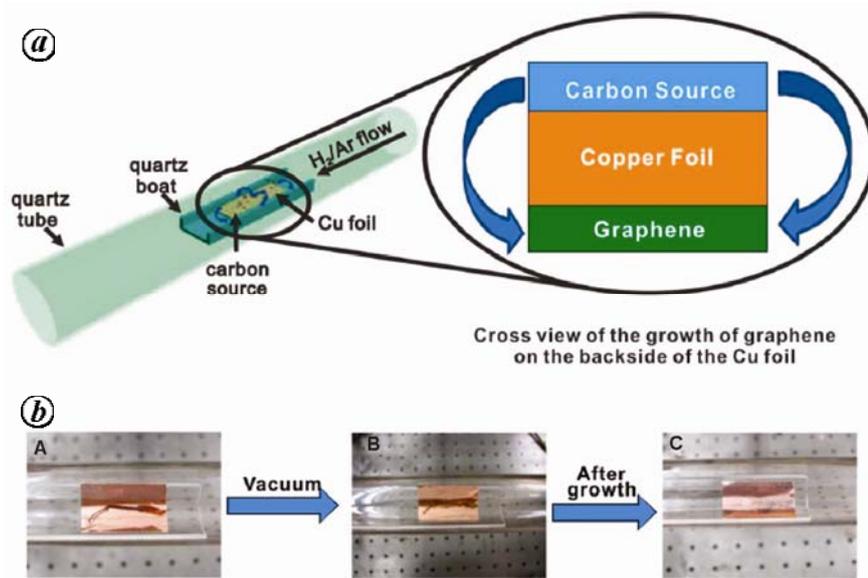


Figure 1. a, Diagram of the experimental apparatus for the growth of graphene from food, insect or waste in a tube furnace. (Left) Cu foil with the carbon source contained in a quartz boat is placed at the hot zone of a tube furnace. The growth is performed at 1050°C under low pressure with a H₂/Ar gas flow. (Right) Cross view that represents the formation of pristine graphene on the backside of the Cu substrate. b, Growth of graphene from a cockroach leg. (A) One roach leg on top of the Cu foil. (B) Roach leg under vacuum. (C) Residue from the roach leg after annealing at 1050°C for 15 min. The pristine graphene grew at the bottom of the Cu film (not shown). Reprinted with ACS permission from Ruan *et al.*⁵. Copyright (2011) from American Chemical Society.

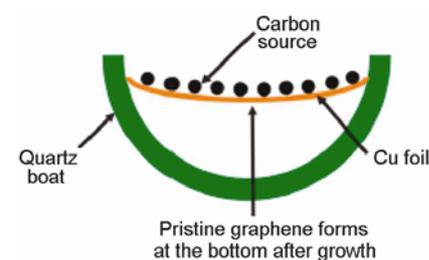


Figure 2. Arrangement of the Cu foil within the quartz boat. The size of the Cu foil was ~2 cm × 3 cm and the boat was 40 cm long and cut from a quartz tube with a 15 mm inside diameter. Reprinted with ACS permission from Ruan *et al.*⁵. Copyright (2011) from American Chemical Society.

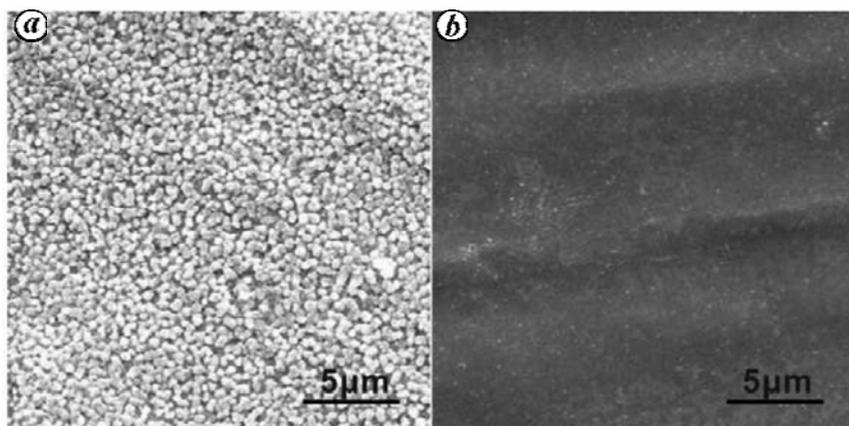


Figure 3. SEM images of the Cu foil after growth of graphene from a Girl Scout cookie. **a**, The original frontside of the Cu foil; there was a large quantity of particle residue after the pyrolysis of the cookie. **b**, The backside of the Cu foil. Reprinted with ACS permission from Ruan *et al.*⁵. Copyright (2011) from American Chemical Society.

and a portion of the carbon diffused to the backside of the Cu foil forming a monolayer graphene film. It is yet to be concluded whether the diffusion is through the Cu foil or via the edges.

Inspection by SEM of both sides of the Cu foil after a growth experiment revealed the presence of many residual particles on the original frontside (Figure 3a), while almost no particles were observed on the backside of the Cu foil where the graphene was formed (Figure 3b). Ruan *et al.*⁵ believe that during growth most of the carbon segments from the decomposition of the solids are carried away as gases by the H₂/Ar flow.

Raman spectra of the produced films have small or no D peaks, and the G and 2D peaks are found at 1585.5–1591.4 and 2682.6–2693.9 cm⁻¹ respectively. The values of full width at half-maximum of the G peak and 2D peak are 14.1–16.3 and 32.0–35.1 cm⁻¹ respectively. In the UV spectra, each film exhibits a peak at 268 nm corresponding to

$\pi \rightarrow \pi^*$ transition for the aromatic C–C bond in graphene and the typical ($2.4 \pm 0.1\%$) absorption at 550 nm. Both Raman and UV spectral studies indicate the monolayer nature of graphene. As most of the carbon sources contain atoms other than carbon, like oxygen, sulphur, nitrogen or phosphorus, Ruan *et al.*⁵ also confirmed from X-ray photoelectron spectral studies that no heteroatoms were present in the monolayer graphene, suggesting its pristine nature. The hexagonal lattice structure of graphene was confirmed by selected area electron diffraction pattern in transmission electron microscopy.

Ruoff and co-workers reported the mechanism of growth of graphene on copper layer from amorphous carbon source¹³. In their experimental set-up a mass spectrometer was included in order to probe the atmosphere change in the tube furnace *in situ* during graphene growth. From their experimental results, Ruoff and his group suggested that gase-

ous hydrocarbons, e.g. CH₄ ultimately yield graphene on copper through reaction of H₂(g) with the amorphous carbon film¹³.

Since Tour and his group have successfully grown high-quality monolayer graphene on one side of the copper coil by decomposition from less expensive carbon sources, one may expect the cost of graphene to drop quickly as commercial interests develop methods to manufacture it in bulk.

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