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High-temperature stability of suspended single-layer graphene

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We report in situ Joule heating on suspended single-layer graphene in a transmission electron microscope (TEM). Thermally-driven degradation of pre-deposited nanoparticles on the membrane is monitored and used for local temperature estimation. By extrapolating the Joule heating power and temperature relation, we find that the suspended single-layer graphene has exceptional thermal stability up to at least 2600 K.

1 Introduction Graphene, an atomically-thin two-dimensional lattice of carbon atoms, has been attracting intense research efforts owing to its superior electronic, mechanical, and thermal properties [1–4]. Graphene exhibits interesting electronic transport properties such as high carrier mobilities and the half-integer quantum Hall effect [1, 2], and displays a high Young's modulus [3]. Suspended graphene has thermal conductivity of about 5000 W/mK [4]. Graphite is stable at very high temperatures (sublimation at around 4000 K) [5] and graphene, or suspended graphene, may also be thermally robust. On the other hand, the two-dimensional nature of graphene may limit its stability. Unfortunately, due to difficulties of preparing suspended graphene samples and the experimental set-up, there has not been an experiment on high-temperature thermal stability of suspended graphene.

Here, we prepare suspended single-layer graphene and perform in situ Joule heating experiments in a transmission electron microscope (TEM) to study the thermal stability of suspended graphene. We estimate that suspended chemical vapour deposition (CVD)-grown graphene is stable at temperatures up to (or exceeding) 2600 K.

2 Experiment and analysis

2.1 Experimental set-up Figures 1a and b show sample preparation and experimental set-ups for in situ Joule heating experiments on suspended CVD-grown graphene. Graphene is synthesized on copper foil by adapting a recent work [6]. CVD growth of graphene on copper can yield large-area graphene of mostly single-layer [6]. We transfer the graphene to a commercial TEM grid (Quantifoil holey carbon film grid) using a recently developed clean transfer process [7]. After the transfer, the TEM grid is cut with a razor blade into small pieces and attached to an aluminium wire with conducting epoxy (Fig. 1a). This sample is inserted into the TEM (JEOL 2010) for in situ experiments. Near the region cut by the razor blade, we locate suspended graphene on the Quantifoil amorphous carbon film (Fig. 1b). The amorphous carbon film gives mechanical support for the suspended graphene. The large area of CVD-grown graphene makes it relatively easy to locate suspended graphene and perform in situ experiments. Using a nanomanipulation platform inside the TEM [8], we make an electrical contact to the suspended graphene with a mobile tungsten probe and induce Joule heating (Fig. 1b).

2.2 Characterization of CVD-grown graphene To confirm that the graphene is single layer, we characterize the CVD-grown graphene by Raman measurement and electron diffraction. Raman measurements are performed using a Renishaw inVia Raman microscope with a 514 nm laser. A laser beam size of about 1 μm is used.

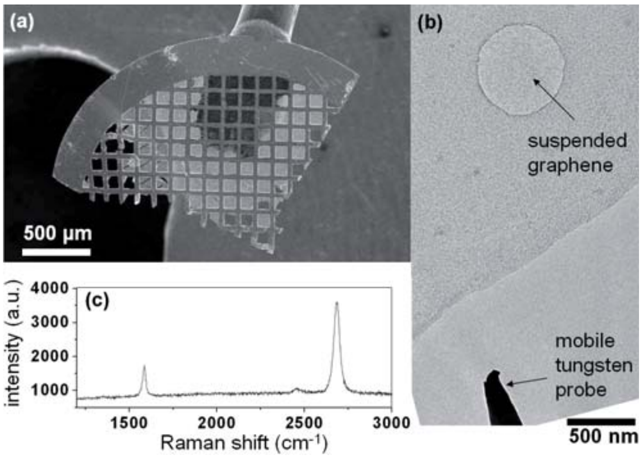

Figure 1 Sample and experimental set-up of in situ Joule heating of suspended graphene. (a) SEM image of a TEM grid (Quantifoil holey carbon film grid), covered with graphene and then cut with a razor blade. The TEM grid is attached to an aluminium wire for insertion to a TEM holder. (b) TEM image of the graphene sample and the mobile tungsten probe for the in situ TEM experiment. Suspended graphene is found inside the holes in the amorphous carbon film. Graphene is contacted by the mobile tungsten probe, and electrical current flows through the graphene. (c) Raman spectrum of CVD-grown graphene transferred to a silicon oxide/silicon substrate.

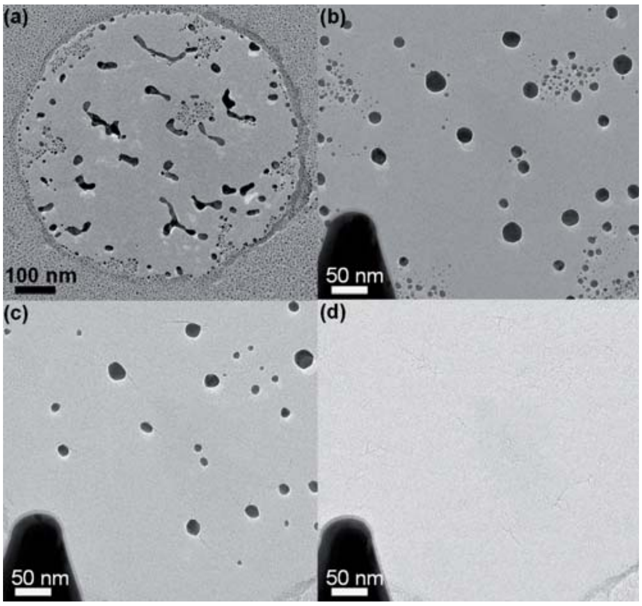

Figure 2 In situ evaporation of pre-deposited Au particles on suspended graphene. (a) TEM image of suspended graphene after Au (nominal thickness of 0.6 nm) is deposited with an e-beam evaporation process. (b–d) Sequential TEM images of in situ evaporation of Au particles on the suspended graphene. (b) TEM image of the Au-deposited graphene after establishing electrical contact with the mobile tungsten probe. The tungsten probe is positioned in the left-lower corner. (c) TEM image as Au particles start to evaporate with Joule heating. (d) TEM image of the graphene after Au particles have completely disappeared.

Figure 1c shows the representative Raman spectrum from graphene which has been transferred to a silicon oxide/silicon substrate. The absence of a D peak shows that the CVD-grown graphene is of high quality. The intensity ratio of 2D and G peaks confirms that the graphene is mostly single layer [6]. The electron diffraction pattern also confirms that graphene is mostly single layer [7].

2.3 Results and analysis We find that the suspended single-layer graphene can be heated up and remain stable at 2600 K (and possibly higher temperatures) with Joule heating. Figure 2a shows the TEM image of suspended graphene after Au is pre-deposited with an e-beam evaporation process. TEM images have been taken with acceleration voltage of 100 keV to minimize the electron beam damage to the sample during the experiments. Using the mobile tungsten probe, we establish electrical contact to the graphene and induce the Joule heating. As we increased the Joule heating power, we observed in situ the evaporation of Au nanoparticles (Fig. 2b–d). From this result, we confirm that the suspended graphene has reached at least 1275 K, the evaporation temperature of Au nanoparticles [9].

Figure 3a shows Joule heating power versus time for the in situ experiment. When the Joule heating power is $P_1 = 0.55$ mW, all the Au particles pre-deposited on graphene have completely evaporated. Later, the graphene was found to be stable with higher Joule heating power, $P_2 = 1.9$ mW.

Our procedure for estimating the temperature of suspended graphene with Joule heating power P_2 is as follows. The exact position of maximum temperature during a Joule

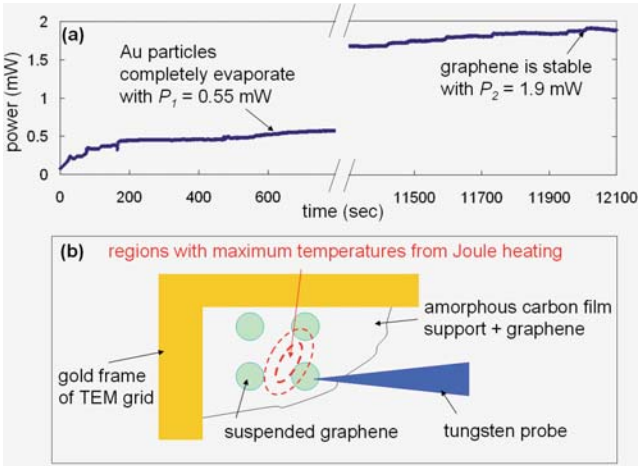

Figure 3 (online colour at: www.pss-rapid.com) Joule heating power data and experimental geometry of the in situ experiment. (a) Joule heating power variation in time during the experiment. (b) Geometry of the in situ Joule heating experiment. Electrical current is flowing from the tungsten probe to the gold frame and inducing Joule heating on the suspended graphene and carbon film. Graphene regions between the gold frame and the tungsten probe reach the highest temperature in the sample.

heating experiment depends on sample geometry and requires knowledge of the thermal and electrical properties of the material (graphene and amorphous carbon film). However, since the gold frame of the TEM grid and the tungsten probe are thermally well anchored and act as heat sinks, the region of maximum temperature in the sample is in the central suspended region of the carbon film and graphene as shown in Fig. 3(b).

We can set an equation from the thermal equilibrium conditions,

$$P_{\text{heating}} - P_{\text{radiation}} = c\kappa \cdot \Delta T\,, \tag{1}$$

where P_{heating} is Joule heating power, $P_{\text{radiation}}$ is power escaping through radiation, c is a sample and experiment dependent constant, κ is the average thermal conductivity of sample between the maximum and minimum temperature region, and ΔT is temperature difference between the maximum temperature, $T_{\max}$, and minimum temperature, $T_{\min}$, in the sample. We can safely assume that the minimum temperature is room temperature, T_r = 300 K (at the tungsten probe and gold frame). $P_{\text{radiation}}$ is estimated by using

$$P_{\text{radiation}} = \int_S \varepsilon\sigma T(S)^4 \,\mathrm{d}S < A\varepsilon\sigma T_{\max}^4\,, \tag{2}$$

where ε is emissivity (assumed to be 1 in the calculation), σ is the Stefan–Boltzmann constant, and S is the surface area of the sample. We can set an upper limit on $P_{\text{radiation}}$, which is $A\varepsilon\sigma T^4_{\max}$, where A is the surface area of the amorphous carbon film and graphene (from the hottest region in the sample). A is estimated as 200 μm^2 from a TEM image in our experiment. The radiation power $P_{\text{radiation}}$ is found to be negligible compared to P_{heating} when $T_{\max}$ is lower than 1500 K.

Putting $T_{\max} = T_1$ = 1275 K and P_1 = 0.55 mW, the reference point deduced from the Au particle evaporation, in Eqs. (1) and (2), we find $c\kappa = 5.6 \times 10^{-4}$ mW/K. Using this $c\kappa$ value and solving Eqs. (1) and (2) with a new Joule heating power, P_2 = 1.9 mW, gives a lower limit for $T_{\max}$ at 2600 K. Since thermal conductivity κ falls due to enhanced phonon–phonon scattering at high temperatures [9], the assumption of the same $c\kappa$ value tends to give lower values in the calculation of $T_{\max}$. Therefore, we conclude that the suspended CVD-grown graphene is stable at temperatures of at least 2600 K.

3 Conclusion We demonstrate that the suspended single layer CVD-grown graphene can be stable at very high temperatures (at 2600 K or higher) via in situ Joule heating experiments. The exceptional temperature stability of suspended graphene may be related to its superior thermal conductivity. Typical TEM heating stages can operate only up to around 1000 K. Even a specialized heating holder can only reach approximately 1400 K [10]. Our in situ Joule heating experimental set-up demonstrates the high-temperature stability of graphene and opens up opportunities for high temperature reaction monitoring beyond the commercial TEM heating stage range.

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