

Supporting Information

Water-mediated and instantaneous transfer of graphene grown at 220 °C enabled by a plasma

Timothy van der Laan^{1,2,3*}, Shailesh Kumar¹ and Kostya (Ken) Ostrikov^{1,2,3}

1. Plasma Nanoscience, CSIRO Manufacturing Flagship, P.O. Box 218, Lindfield, New South Wales 2070, Australia

2. Complex Systems, School of Physics, The University of Sydney, New South Wales 2006, Australia,

3. School of Chemistry, Physics, and Mechanical Engineering, Queensland University of Technology, Brisbane, Queensland 4000, Australia

*e-mail: Tim.Vanderlaan@csiro.au.

This Supplementary Information includes:

S1: Plasma-specific effects

S2: XRD analysis of plasma modification of catalyst surface (S3-S6)

S3: EBSD analysis of plasma treated and untreated Cu foil (S7)

S4: Videos of water-mediated transfer of graphene (V1 & V2)

S5: Video of the wetting of Cu foils (V3 & V4)

S6: Comments on potential industrial scalability

S7: Table comparing our plasma based process to standard thermal CVD

S8: Transferred films on other surfaces

S9: Catalyst Reuse

S10: Electrical characterization set-up

Figures S1 – S9

Videos V1 – V4

S1: Plasma-specific effects and competitive advantage

Plasma-specific effects

Firstly the gaseous discharge causes breakdown of methane (which is considered the rate limiting step in graphene synthesis) in the gas phase compared to thermal processes where this process is primarily catalytically activated at high temperatures. This breakdown also produces a wide plethora of available carbon species that may be used in the construction of graphene with a considerable proportion of radicals and ions not commonly found in CVD processes¹. At elevated temperatures complex hydrocarbons are stabilised in preference to methane². Here the plasma-related effects rather than purely thermal effects facilitate the generation of these species. In the temperature range of our interest (below 300 degrees on the catalyst surface) thermal dissociation of methane (and also of the more stable hydrocarbons) is ineffective making low-temperature synthesis of graphene unlikely in a conventional thermal CVD process. In the plasma case one has the required building units at these low temperatures making graphene growth possible.

Another beneficial property of the plasma is the activation of a surface when it is exposed to the plasma. This occurs as energetic bombardment of species from the plasma cause re-ordering of bonding on the exposed surface. In this case as the copper is exposed to the plasma there will be an increase in dangling bonds, nanoscale roughness of the catalyst and other nanoscale effects that will serve to increase the overall energy of the surface. This may lead to enhanced stability of graphene on the surface as it has a high surface energy and so the energy cost of covering copper with a high energy surface will be reduced when the copper is activated. The plasma based activation of a surface also leads to longer range

movement of species on the surface compared to the neutral case and allows the nucleation of complex nanostructures.

The only source of heating in this process is the plasma itself. When a plasma is used as the heating source most of the heat is localised to the surface exposed to the plasma. Thus the heating of the entire chamber (even the entire catalyst) is not needed. In fact, the plasma heating is supplied directly to the area of the surface where the graphene grows. The energetic ion bombardment also cause an increase in the thermal energy at the site of impact and not over the entire surface meaning that this heating is targeted and not wasteful³. It is also possible to apply the heating predominantly to the surface areas where new species are impinging rather than over the entire surface.

Finally, the plasma-specific advantages are also seen in the synthesis of other carbon nanostructures. The large amount of atomic hydrogen produced in this type of system has been shown to be beneficial in the synthesis of sp^2 hybridised carbon structures. This is seen by the selective etching of atomic hydrogen of sp^3 and amorphous carbon instead of sp^2 carbon structures⁴. Argon mediated defect healing is also possible in the plasma which has shown to allow localised remodelling of growing carbon structures reducing defects in their structure⁵.

Lastly, we have non-equilibrium plasmas which are primarily controlled by kinetic processes. Considering the growth of graphene on copper at low temperatures, it is thus likely that kinetic rather than thermodynamic processes drive the growth. Consequently, a kinetically-driven plasma system which in turn drives kinetic processes on the surface is likely to be beneficial.

S2: XRD analysis of plasma modification of catalyst surface

Below is a set of XRD spectra taken on a plasma treated and untreated copper foil and for the plasma treated foil at varying incident angles. These spectra demonstrate that the modification of the copper foil is predominantly on the surface which has been discussed in the main text of the paper.

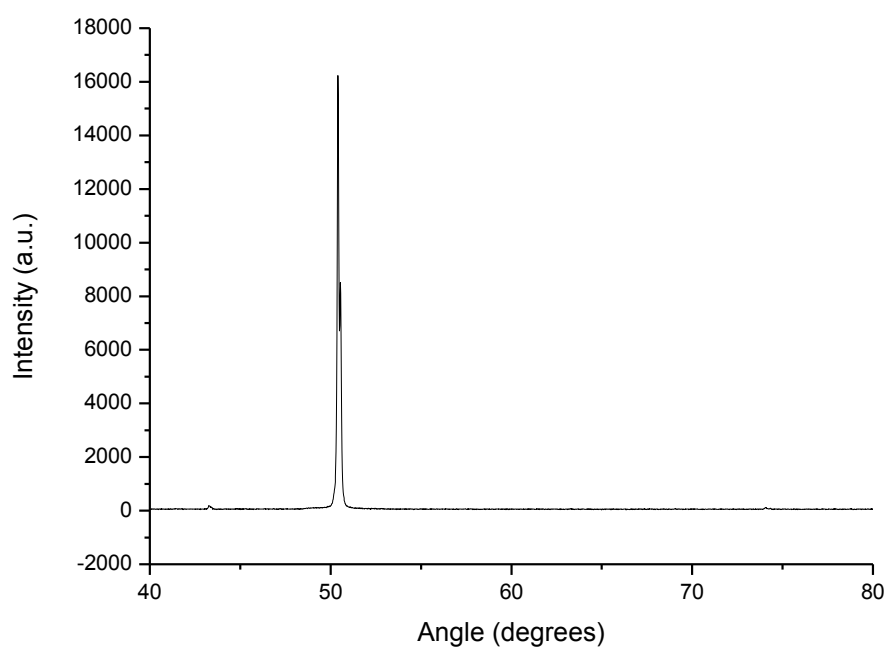


Figure S1: θ - 2θ scan of the untreated copper foil

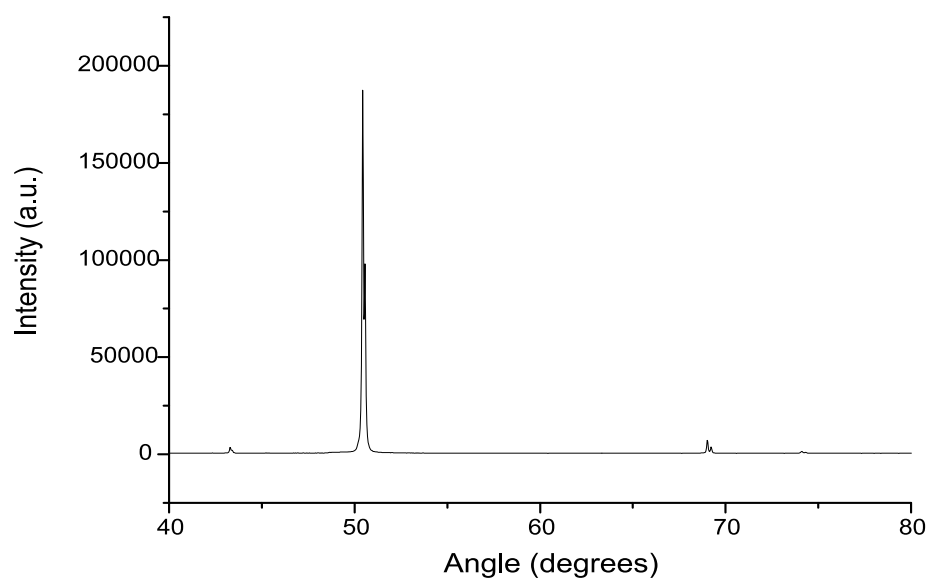


Figure S2: θ - 2θ scan of the plasma treated copper foil

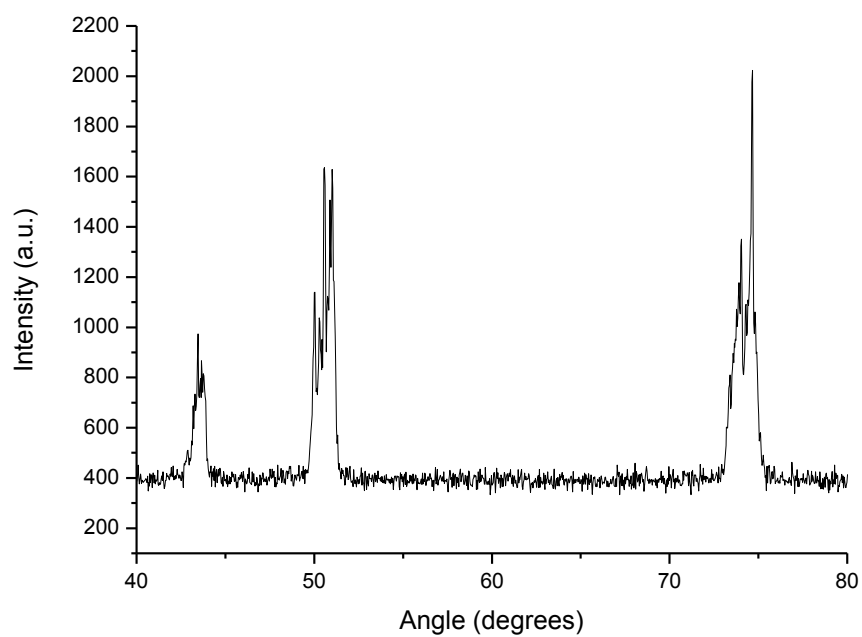


Figure S3: Grazing angle scan of plasma treated copper at 5°

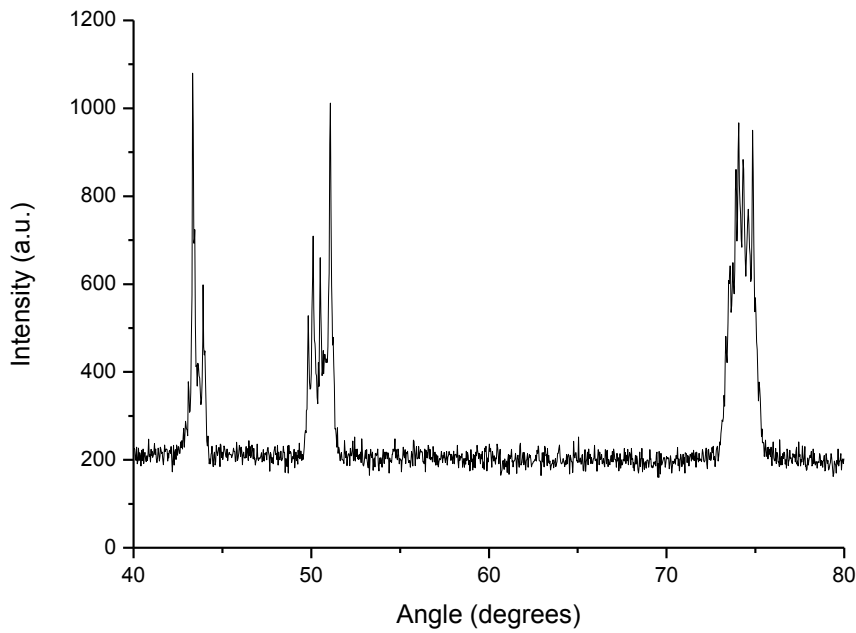


Figure S4: Grazing angle scan of plasma treated copper at 2°

Comparing S3 and S4 there is an obvious change as two new peaks emerge. In this case the Cu(101) and Cu(111) phases are responsible for the peaks and thus it can be concluded that there is more 101 and 111 crystal phase alignment in the plasma treated versus the untreated Cu foil.

Further from figures S4-S6 we can conclude that as we decrease angle and probe a shallower section of the copper surface the Cu(200) peak becomes less dominant. For this reasons we conclude that changes in the crystal orientation of the copper are largely confined to the surface of the copper.

S3: EBSD analysis of plasma treated and untreated Cu foil

Here we include further EBSD analysis complementary to that which is included in the text.

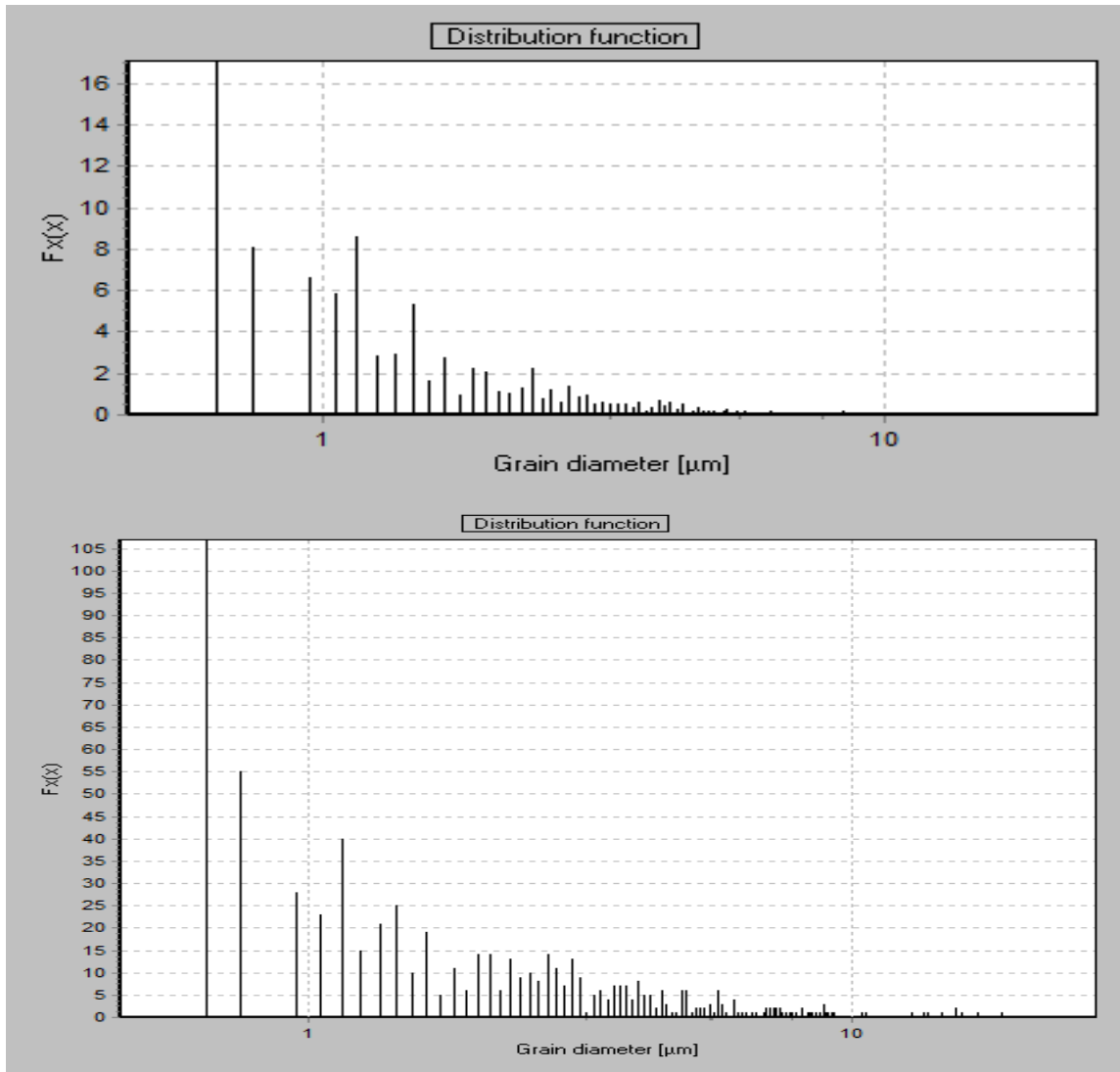


Figure S5: Grain size distribution on plasma treated (top) and untreated (bottom) Cu foil.

From the distribution functions of the grain sizes present in the 2 Cu foils we support our claim in our paper that upon the plasma treatment the grain size is drastically modified. More specifically, we see a more even distribution of grain sizes in the plasma treated foil whilst in the untreated case we see a much greater contribution from smaller-size grains.

S4: Videos of the water-mediated transfer of graphene

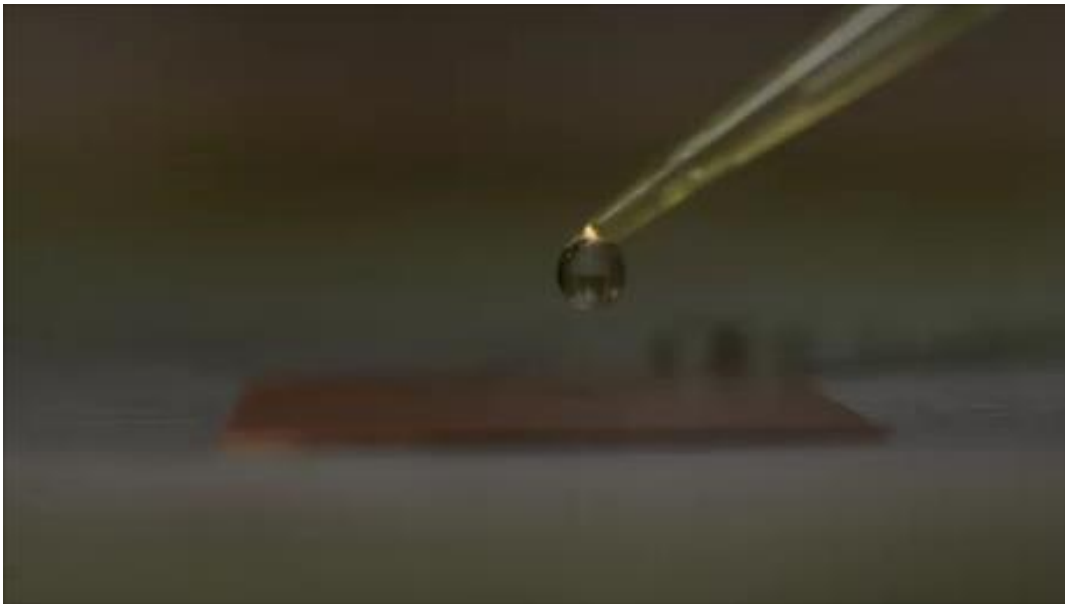


Video V1: Video of the lifting of the graphene film from the Cu foil catalyst.

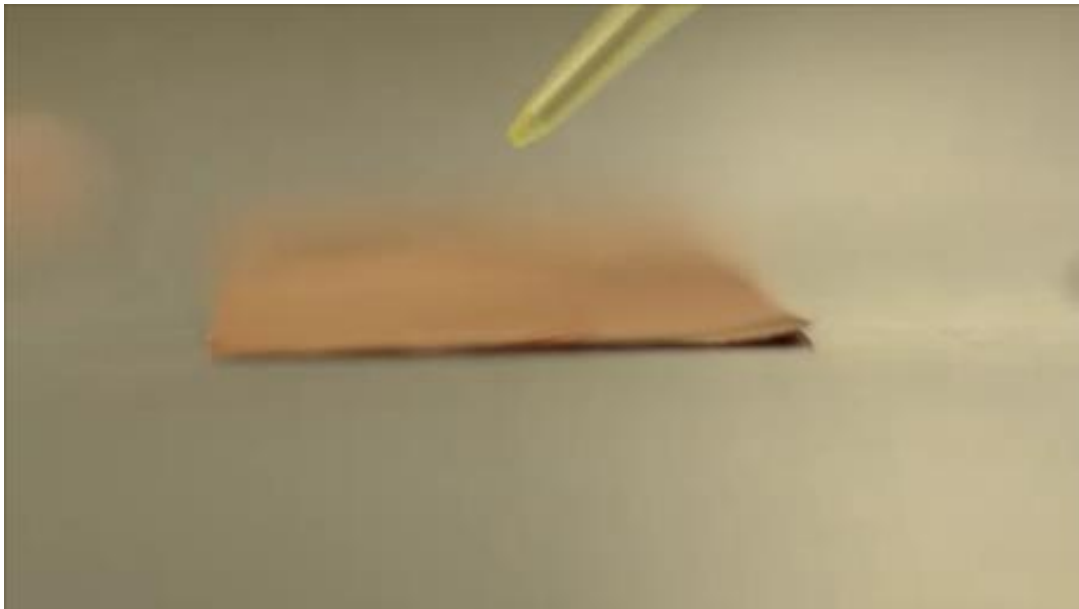


Video V2: Video of the transfer of the GF lifted off the Cu foil onto a piece of plastic.

S5: Video of the wetting of Cu foils



Video V3: Video of water droplets placed on an untreated Cu foil and the subsequent wetting of the foil.



Video V4: Video of water droplets placed on a plasma treated Cu foil and the subsequent wetting of the foil.

S6: Comments on potential industrial scalability

Here we make a short statement on the potential up-scaling of this plasma process to an industrial level. Plasma processes are wide spread in industrial setting including but not limited to etching, sputtering, implantation, sprays, chemical production and sterilisation. One of the biggest industries implementing plasma processes is the semiconductor industry. Eventually with on device synthesis of graphene in mind the use of in line plasmas like those used by semiconductor manufacturers may prove ideal. There is a large body of literature where more details about the present-day industrial plasma-based processes can be found. Specifically regarding the case of the films we produce, we notice no discernible loss of homogeneity across the sample. We use a 3x3cm catalyst for the experiments discussed in this report however we can and have already grown on catalysts ~8x5cm. Whilst this does not make the case for our work being immediately implemented in large scale fabrication it does show that the process is scalable.

S7: Table comparing our plasma based process to standard thermal CVD

Thermal Chemical Vapour Deposition (TCVD)	Plasma Chemical Vapour Deposition (PCVD)
Wasteful system heating	Direct surface heating
High Temperatures (~1000 °C)	Low Temperatures (as low as 220 °C)
Long heating, dwelling and cooling times	Growth carried out in minutes
Breakdown of precursor on catalyst	Plasma phase breakdown as well as on catalyst
Very few controllable parameters	Greater control through plasma effects
Loss of catalyst	Catalyst can be cleaned and reused
Slow, toxic chemical based transfer	Instantaneous, water-mediated transfer

S8: Transferred films on different surfaces

Here we show that the surfaces that the graphene we produce can be transferred to are not limited just to the glass shown in Figure 3. In fact we can, and have transferred the films to plastics, paper and cotton all shown below in Figure S6.



Figure S6: Graphene transferred to a) plastic, b) paper and c) cotton.

We also include an SEM image of the graphene synthesized in this plasma process this film is on a glass surface. The structure of the film after our water-based transfer is shown. The film appears to be made up of a number of small grains that sit on top of each other and thus provide structural integrity to the whole film during transfer.

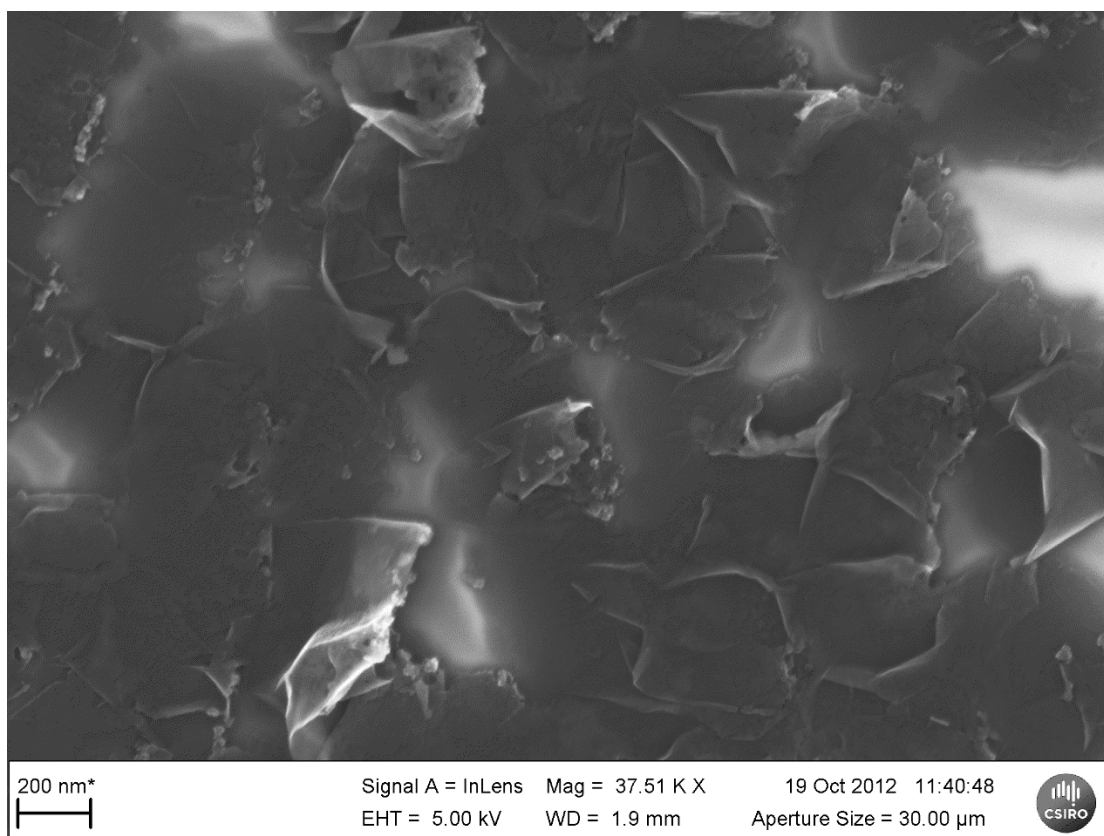


Figure S7: SEM image of the film after transferring to glass demonstrating the films structure.

S9: Catalyst Reuse

Figure S8 as a representative Raman spectrum from a sample prepared using exactly the same conditions as those in the methods section of the manuscript. The difference however is that the Cu foil used in this case was one that had previously been used to grow graphene. There was no preparation of the foil it was only left to dry in air after transfer of the previous graphene film. There is a small difference in the D/G and 2D/G ratios between the reused and unused Cu catalysts (in this case a slightly stronger D and a weaker 2D peak). The peak ratios however can be improved through plasma (Ar/H₂) exposure before injecting methane effectively cleaning the Cu surface and preparing it for graphene growth. The exact interactions are however beyond the scope of this work.

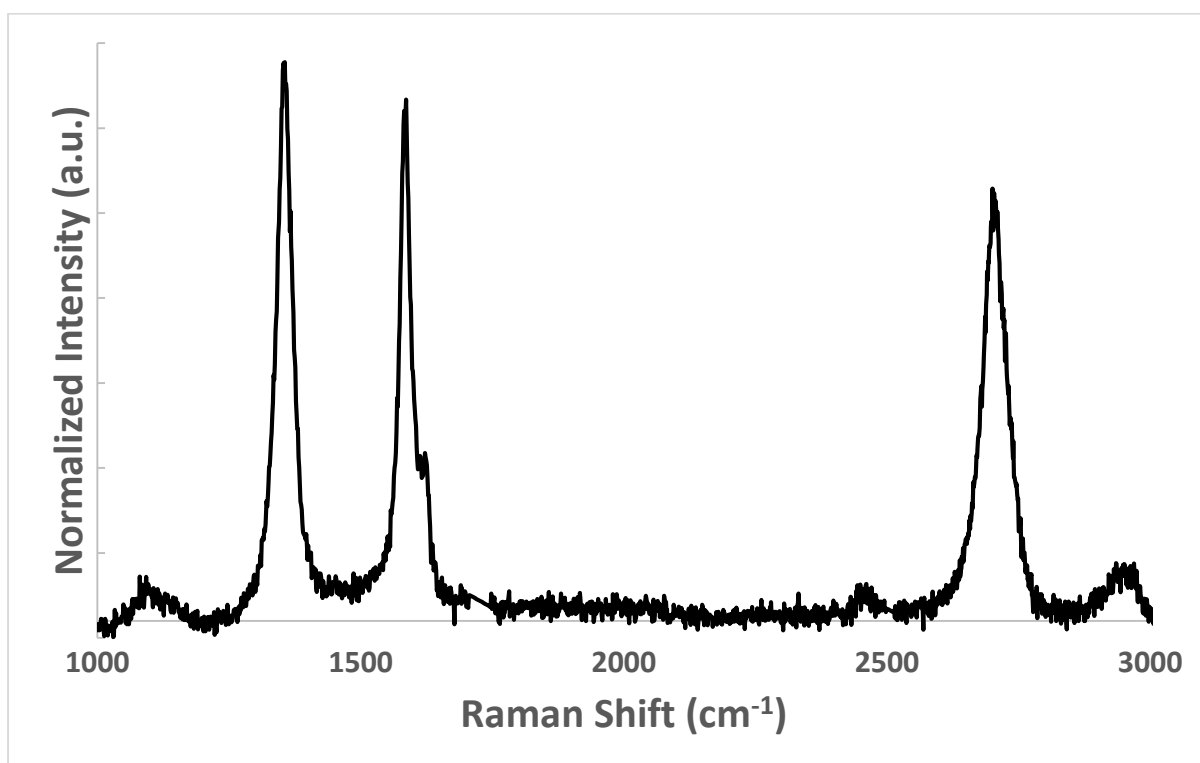


Figure S8: Raman spectrum from graphene film grown on a previously used Copper catalyst.

S10: Electrical characterization set-up

Figure S9 shows the results of the Hall effect measurements. The slope from this plot is used to determine the charge carrier concentration. Figure S10 shows the fabricated device. A current is supplied from left to right and the voltage is recorded from top to bottom of the image. A magnetic field is applied perpendicular to the current and the film in both a positive and negative direction. The changes in the voltage as the magnetic field is varied is then used to extract the charge carrier type and concentration.

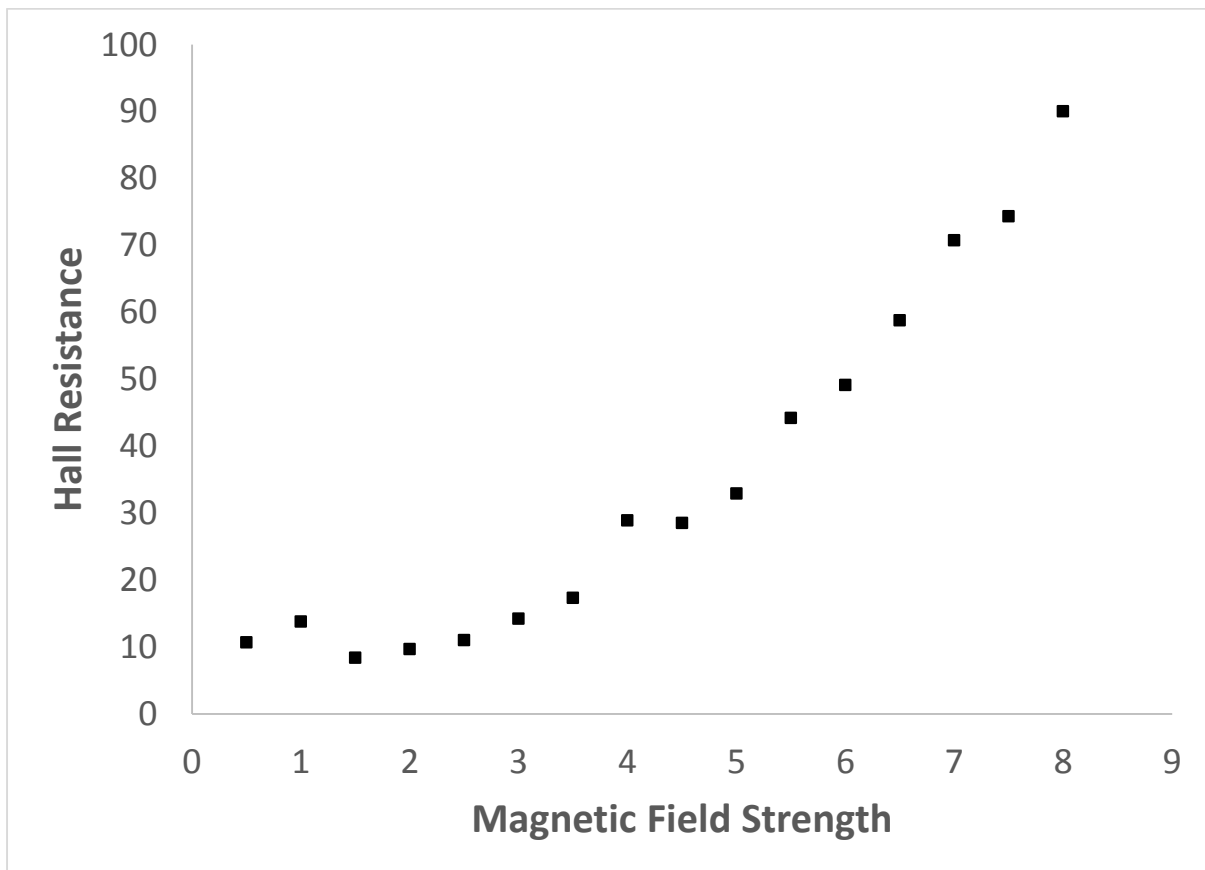


Figure S9: Hall effect measurements showing the Hall resistance versus magnetic field strength.

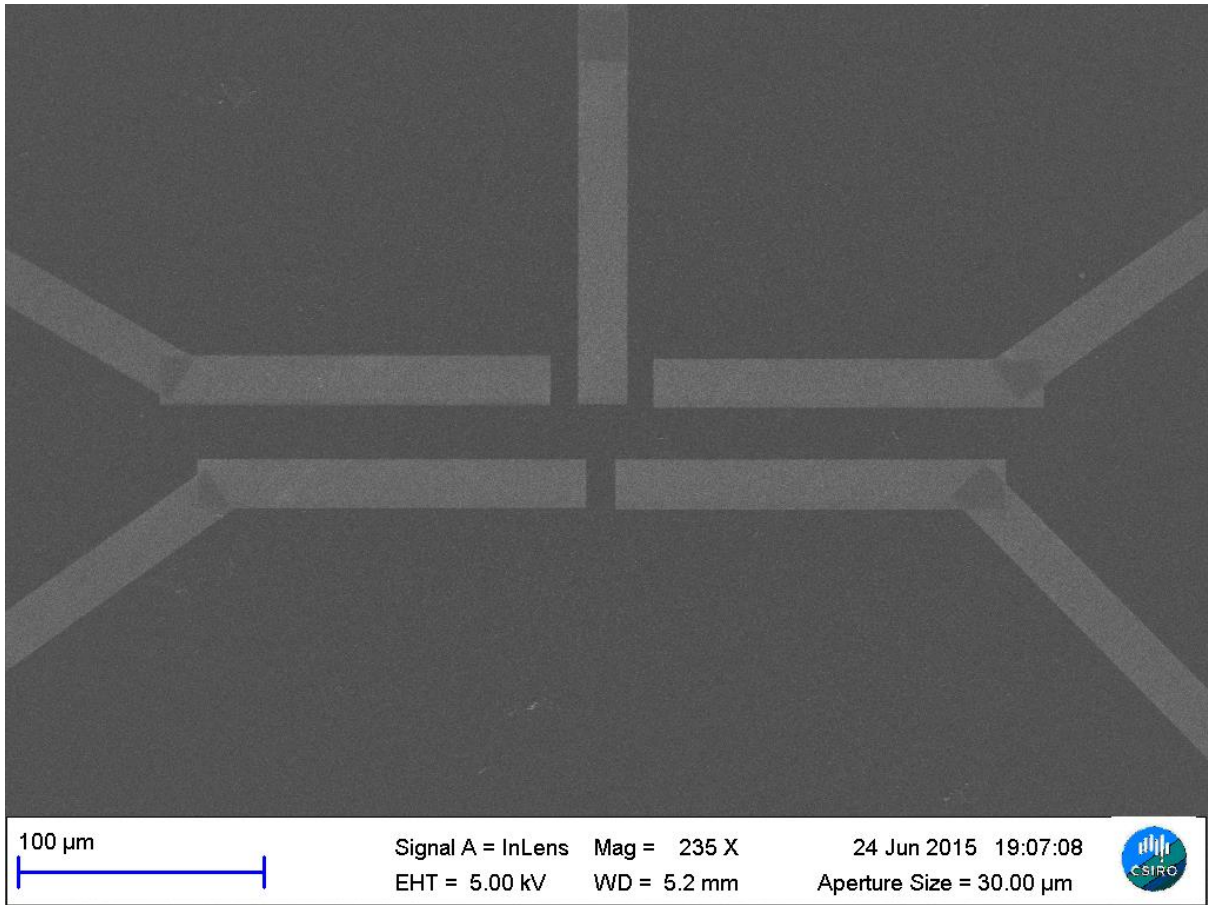


Figure S10: Image of the fabricated device for Hall measurements

References

1. I. Denysenko, K. Ostrikov, M. Yu and N. Azarenkov, *Journal of Applied Physics*, 2007, **102**, 074308.
2. Z. Li, W. Zhang, X. Fan, P. Wu, C. Zeng, Z. Li, X. Zhai, J. Yang and J. Hou, *The Journal of Physical Chemistry C*, 2012, **116**, 10557-10562.
3. K. B. K. Teo, D. B. Hash, R. G. Lacerda, N. L. Rupesinghe, M. S. Bell, S. H. Dalal, D. Bose, T. R. Govindan, B. A. Cruden, M. Chhowalla, G. A. J. Amaratunga, M. Meyyappan and W. I. Milne, *Nano Letters*, 2004, **4**, 921-926.
4. M. Zhu, J. Wang, R. A. Outlaw, K. Hou, D. M. Manos and B. C. Holloway, *Diamond and Related Materials*, 2007, **16**, 196-201.
5. E. C. Neyts, Y. Shibuta, A. C. van Duin and A. Bogaerts, *ACS Nano*, 2010, **4**, 6665-6672.