Structured Graphene – Spinnable CNT and Beyond

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Graphene, a hexagonal lattice of carbon only a single atom thick, is attracting immense interest due to its exceptional properties of electrical conductivity, thermal stability, and mechanical strength as well as its unique electronic properties. Many potential applications such as nano-scale electronic devices, sensors and interconnects need graphene structures with well-controlled feature size and tuneable electronic properties, such as arrays of graphene 'nano-ribbons', 'nano-grids' and 'nano-struts' as a means of assembling the new nano- materials. Also required are structures to increase surface area or structural stability of graphene films, for example to produce dye-sensitised and flexible-organic solar cells.

A range of methods have been used to produce patterned or structured graphene, including photolithography, direct laser writing, micro-contact printing as well as the direct growth of graphene on pre-patterned catalyst substrates. For example Kim et al[1] evaporated Ni through a mask on to a Si/SiO_2 substrates to make circular- and strip-patterned graphene for integrated devices.

We have developed a simple and efficient process to produce freestanding graphene membranes patterned and reinforced with highly aligned 'Directly Spinnable Carbon Nanotube (DSCNT) web', also produced in our laboratory. The DSCNT are specially grown CNT forests that can be drawn (spun) directly from the growth substrate as a continuous web which can be used directly or twisted into a yarn. The web provides the carbon for graphene growth as well as reinforcing and patterning the surface structure. We have also used commercial Cu TEM grids with different grid patterns alone and in conjunction with DSCNT and copper foil to create a range of self supporting graphene (Figure 1) structures.

The DSCNT was prepared according to our published methods[2] and, from this; up to six layers of highly aligned web was laid down on a pre-annealed copper substrate. Graphene was grown using a CH_4 as the carbon source[3]. It is also possible to adjust conditions to utilise carbon from the DSCNT structure, and this method is being developed further. Commercial Cu TEM grids were annealed either in direct contact with the copper substrate or placed on top of the DSCNT layer prior to Graphene synthesis (Figure 1).

Raman spectroscopy of graphene produces two major peaks and one minor[4]. The D peak at 1350 cm^{-1} is associated with disorder and is very weak in a single graphene sheet away from edges. The G peak at ~1580 cm^{-1} is usually weak and narrow for single layer graphene, growing with number of layers to be the largest peak in graphite. The 2D band at ~2700 cm^{-1} is very sensitive to the number of graphene layers in the sample, broadening and developing a second peak at higher wavenumbers. There is some correlation in the intensity of G/ 2D peak height with number of layers up to about 5. We find by Raman (514 nm) (figure 2) that from our process with methane but without the DSCNTs, we grow about three layers of graphene. This is confirmed by TEM (Figure 3c & 3d) which shows three or 4 layers of graphene in the plain graphene sample. Raman analysis (Fig 2) of the graphene structures with DSCNTs show more graphite character as they are about 7 shells thick and so appear more disordered. Removal of excess (XS) DSCNTs gives a Raman spectrum more comparable to the pure graphene. The DSCNT web is seen (Fig 3a & 3b) to have blended into the graphene surface structure and modelling and further analysis are being conducted to understand the geometry of this connection.

Placement of Cu TEM grids on a copper substrate followed by annealing (Fig 1) results in the grid being firmly bonded to the substrate. Where the grid edges are in close contact, a smooth boundary transition to the substrate results, whereas if the grid edge is separated, it remains distinct. A TEM grid placed on a layer of DSCNT and annealed suffers major distortion. Graphene grown on the TEM / copper substrate follows the geometry of the combined structure.

References

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Figures

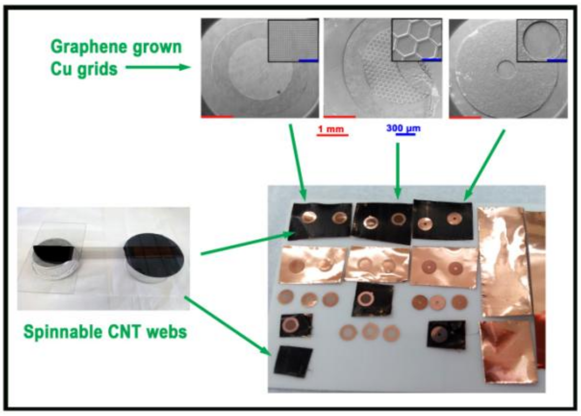

Fig.1 - Showing spinnable CNTs and Cu grids on top of Cu foils.

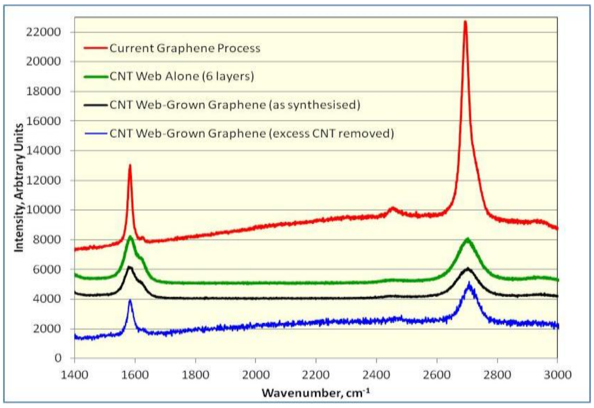

Fig. 2 – Raman spectra of spinnable CNT , Web-Grown spinnable CNT graphene and graphene on Cu foil

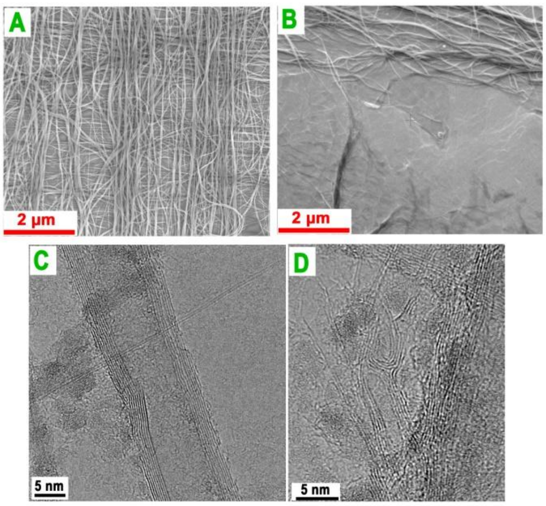

Fig.3- SEM of DSCNT crossed web (A), Cu substrate coated with graphene that has been patterned by CNT during growth (B, CNT has been removed), TEM of 10 nm diameter CNT and 3 layers graphene (C) and TEM of graphene footprint of CNT (D). The wavy circular patterns are typical ‘ghosting’ of the CNT webs