Covalently bonded carbon nanotube – graphene hybrid material

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We have witnessed tremendous growth in the area of nanomaterials for the past three decades. The discovery of fullerences by Kroto et al. in 1985, was followed by the isolation of some more novel carbon nanomaterials, new allotropes of carbon. These include carbon nanotubes (CNTs) obtained by Iijima in 1991 and graphene isolated by simple exfoliation of graphite with a scotch paper by Novoselov et al. in 2004. These new carbon allotropes are bonded by sp² carbon atoms.

CNTs are ultra-thin carbon fibres with nanometre size diameter and micrometre size length. In 1991, Iijima obtained only multi-walled carbon nanotubes (MWCNTs). Subsequently, Iijima and Ichihashi, and Bethune et al. reported the production of single-walled carbon nanotubes (SWCNTs). On the other hand, graphene is a single atomic layer of graphite and the carbon atoms are linked by sp² bonding. Both SWCNTs and graphene exhibit outstanding and unsurpassed properties like excellent electrical conductivity and large specific surface area (SSA). Theoretical studies of electronic transport between graphene layers covalently connected by CNTs suggest that these outstanding properties will also be extended in three dimensions and will be useful in energy storage and nanoelectronics. Therefore, the interest to obtain a hybrid of these two carbon nanomaterials is not surprising as this provides an approach to extend the spectacular properties of the two carbon allotropes into three dimensions. As the conditions for growth of graphene and CNTs are entirely different, it is certainly a challenging task to assemble CNTs and graphene in the form of a hybrid film with covalent bonding. Though some reports describe synthesis of CNT–graphene hybrid nanostructures, they have not addressed how the two nanomaterials are linked. Further, such hybrid films consisted of overlapped thick graphene aggregates with poor controllability of the nanoarchitecture, resulting in the reduction of the total surface area of the hybrids. Paul et al. reported the fabrication of pillared graphene nanostructures consisting of stacked CNT pillars on large area graphene layers for possible applications in hydrogen storage and supercapacitors. These authors opine that the highly crystalline interface between the CNT pillar and graphene floor confirmed the seamless contact between the two carbon allotropes. The recent report of synthesis of graphene–MWCNT hybrid nanostructure for employing it as an anode for lithium ion batteries by Vinayan et al. yields a hybrid composite. Lee et al. fabricated carbon hybrid films composed of vertical CNTs grown on graphene films. These experimental studies, however, have not unequivocally established whether there are covalent bonds that seamlessly link the CNTs and graphene. However, Nasibulin et al. have obtained a new carbon hybrid in which fullerences are covalently bonded to the outer surface of SWCNTs, and called the new hybrid nanobud.

In a recent article, Zhu et al. have demonstrated the fabrication of CNT (single-walled, double-walled and triple-walled CNTs)–graphene hybrid in which the two materials are shown to be linked seamlessly by covalent bonding. To create the hybrid material, in a joint effort scientists from USA and China began with a copper foil coated with a single layer of graphene by chemical vapour deposition or solid carbon-source growth. This was followed by the deposition of iron catalyst and alumina buffer layer on the graphene in series by electron beam (e-beam) evaporation. A CNT carpet was directly grown from the graphene surface as shown in Figure 1d. It has been observed from SEM images that during growth, the catalyst and alumina are lifted up and the CNT carpet is grown directly out of the graphene resulting in seamless covalent bonds between the graphene and CNT carpet. It is also astonishing to note that the nanotubes growth can be as long as 120 μm (0.120 mm) in 10 min with the formation of single-, double- and triple-walled CNTs on graphene as revealed by SEM images. The various steps in the growth of the hybrid are detailed in Figure 1. SEM images and Raman spectral studies of the hybrid (on Si/SiO₂) confirmed the formation of CNT carpet on graphene layer.

To study the nature of binding in CNT–graphene junctions, Zhu et al. employed an aberration-corrected scanning transmission electron microscope (STEM). Both conventional TEM (Figure 2a, b) and bright field (BF) STEM images (Figure 2c, d) of CNT root region where they link to graphene are shown in Figure 2. In spite of the fact that the CNTs are triple-walled and double-walled in Figure 2c and d respectively, additional shells are found. They may be advantageous for lifting the alumina layer. A close examination of Figure 2e–h reveals that the lateral layers inside the CNTs (shown by cyan colour

**Figure 1.** Scheme for the synthesis of carbon nanotube (CNT) carpets directly from graphene. a. Copper foil substrate. b. Graphene is formed on the copper foil by chemical vapour deposition (CVD) or solid carbon-source growth. c. Iron and alumina are deposited on graphene-covered copper foil using e-beam evaporation. d. A CNT carpet is directly grown from the graphene surface. The iron catalyst and alumina protective layer are lifted up by the CNT carpet as it grows. (Reproduced from Zhu et al. with permission from Nature Publishing Group.)
in Figure 2f, h) are open-ended at the bottom. The observed large Brunauer–Emmett–Teller SSA (2000–2600 m$^2$ g$^{-1}$) is also in support of open-ended CNTs. By recording additional experimental STEM images, Zhu et al.\textsuperscript{11} also confirmed that a ring-like structure is a characteristic property for covalent bonds between CNTs and graphene. A possible model as shown in Figure 2i has been suggested for the CNT–graphene junction\textsuperscript{11}.

The proposed model indicates that the outermost shell of the nanotube root will be bonded to the topmost layer of graphene, which was also directly observed in the annular dark field (ADF) STEM image in Figure 2j. Proof of the hybrid nature of the material lies in the seven-membered rings at the transition from graphene to nanotube, a structure predicted by theory for such a material (Figure 2k and l) and confirmed through STEM images with subnanometre resolution\textsuperscript{11}.

The covalent binding between the two carbon nanomaterials will enable efficient electrical contact between CNT carpet and the graphene layer. This hybrid may be the best electrode interface material possible for many energy storage and electronics applications. The electrical behaviour of CNT–graphene junctions has been studied with devices as shown in the SEM inset of Figure 3a and the $I$–$V$ plots are also depicted in Figure 3a. The measurements were carried out as illustrated in Figure 3b. $I$–$V$ responses were obtained for three types of measurements (Figure 3b): (I) In one experiment micromanipulated probe tip was placed on the Pt electrode and the second tip was shifted horizontally to the CNT carpet electrode. While no current was passing in measurement (II), the current–voltage curves in measurements (I) and (III) are almost identical (Figure 3a). This points out an ohmic contact at the junction of the CNTs and graphene and may also be taken as an evidence for seamless contact between CNT and graphene. This new hybrid material enjoys both high electrical connectivity and large SSA. According to Zhu et al.\textsuperscript{11}, the CNT–graphene hybrid material appears to offer great potential for electronic components like fast supercapacitors because the massive surface area may hold a great deal of energy in a tiny package. The performance of supercapacitors was then elevated and no current was passing through the device (Figure 3a). (III) The second tip was shifted horizontally to the CNT carpet electrode.

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A new CNT–graphene hybrid material has been fabricated and it has been established by aberration-corrected STEM studies the presence of conjugated covalent bonds in the junction between CNTs and graphene. Since the stand-alone properties of the two materials are not affected, the material is endowed with large surface area and high electrical connectivity. These properties will be of immense use in fabricating new electronic devices and in energy storage.


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