Do Damascus swords reveal India's mastery of nanotechnology?

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The exciting discovery of Buckminsterfullerene, C_{60}, during laser ablation of graphite in a pulsed jet of helium by Smalley and co-workers[1], resulted in the addition of another allotrope of carbon, the third form of this element in 1985. As laser ablation method could not produce more than a few tens of thousands of this special new molecule, the electric-arc discharge method was proposed[2], and this has been widely employed for large-scale preparation of fullerenes. This arc-discharge is carried out keeping the gap between the carbon electrodes at about 1 mm in an inert atmosphere and from the collected soot, the fullerenes are isolated.

A careful examination of the carbon cathode used in the arc-discharge process by Iijima[3] resulted in the historical discovery of carbon nanotube (CNT), the name of ultra thin carbon fibre with nanometre-size diameter and micrometre-size length. Iijima obtained only multi-walled carbon nanotube (MWCNT) and that is indeed a milestone in the study of different forms of carbon. Subsequently, Iijima and Ichihashi[4] and Bethune *et al.*[5] reported the production of single-walled carbon nanotubes (SWCNT). CNTs have been recognized as the quintessential nanomaterial and have acquired the status of one of the most active fields of nanoscience and nanotechnology. The MWCNT is composed of 2 to 30 concentric graphitic layers, the diameters of which range from 10 to 50 nm and length to more than 10 μm. On the other hand, SWCNT is much thinner with diameters ranging from 1.0 to 1.4 nm.

CNTs are strong and their Young's modulus is almost 6 to 10 times that of steel. Tensile strength of CNTs is about 20 times higher than that of steel. Thus CNTs are strong, even though they are light. However, they buckle like straw, but do not break and can be straightened without any damage. What is the connection between CNTs and Damascus swords?

Swords were used as weapons in the battlefield till the 19th century and Damascus swords were used in crusades against muslim nations in Europe. Several reasons are attributed to the name Damascus swords. It refers to swords forged in Damascus, Syria. Another reason is that the swordsmith, Damasqui made this type of blade. In Arabic, 'damas' refers to the surface pattern of moiré ripples, which resemble turbulent water, and this is also found in some Damascus swords (Figure 1). These swords have been made during the period AD 900 to the early AD 1800. Some of the swords are kept in museums like the Berne Historical Museum, Switzerland. It is claimed that a Damascus steel blade could cut a piece of silk in half as it fell to the ground. The beautiful Damascus sword has a wavy pattern on its surface and looks like wood grain. Damascus swords are much valued because of their mechanical strength, flexibility and sharpness[6]. In the production of steel, if iron is loaded with up to 2% carbon, hard and brittle steel will be produced, while soft and malleable steel is obtained by the addition of about 0.5% carbon. The Damascus steel is both hard and malleable. These features are important – hard to hold an edge once sharpened, but malleable so that it would not break when hitting other metal in combat. The blades of these swords can be bent to about 90°. It is learnt that the swords were prepared by forging small cakes of steel called *wootz* steel manufactured in southern India and exported to other countries.

Wootz steel was one of the advanced materials of the early period exhibiting properties such as superplasticity and high impact hardness. The recipe for the manufacture of *wootz* steel was an enigma. In the Indian method of preparation of *wootz* steel cake, it is believed that particular ingredients were essential, like wood from *Cassia auriculata* and leaves of *Calotropis gigantean* and ores from particular mines. The production of this type of steel almost vanished possibly because of the depletion of the particular ores. The smiths repeatedly heated and hammered the cake till it was stretched and flattened into a blade. During this process the wavy pattern was formed on the surface of the blade. Verhoeven found that the swords contained a band of iron carbide particles, Fe_3C, known as cementite. It is a mystery how the inherent brittleness of cementite was overcome by Indians in their preparation of *wootz* steel. Success eluded the hands of European swordsmiths to produce steel similar to *wootz*. Recently, Vorhoeven produced a steel which when forged into a blade had all the characteristics of the Damascus blade[7,8]. Their recipe includes iron, carbon and other elements in trace amounts such as vanadium and molybdenum (which are referred to as impurity elements) in addition to rare-earth elements.

The high mechanical properties and flexibility features of Damascus blades resemble those of CNTs. These characteristics probably motivated Reibold *et al.*[9] to probe whether a genuine Damascus sabre contains CNTs, using high-resolution transmission electron microscopy (HRTEM). A specimen was taken from one of the swords kept in Berne Museum and dissolved in hydrochloric acid. The remnants, examined by HRTEM, revealed the presence of MWCNTs with the characteristic distance of 0.34 nm and also bent CNTs (Figure 2 *a* and *b*). Figure 2 *c*

Figure 1. ***a***, Damascus sword; ***b***, Wavy pattern on the sword.

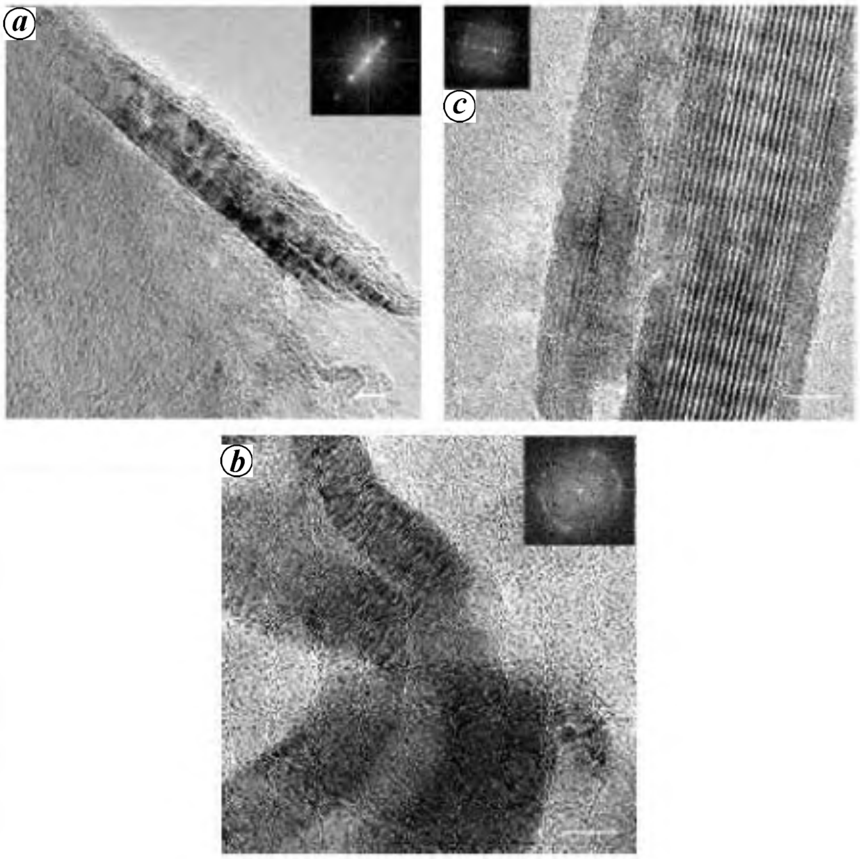

Figure 2. HRTEM images of remnants from dissolution of a sample of genuine Damasus sabre in hydrochloric acid. ***a***, ***b***, MWCNTs with the characteristic distance of $d = 0.34$ nm. In (***b***) the tubes are bent like a rope. ***c***, Remnants of cementite nanowires encapsulated by CNTs, which prevent wires from dissolving in acid. Scale bars: 5 nm (***a***) and (***c***) and 10 nm (***b***) (reproduced from Reibold *et al.*[9] with permission from P. Paufler).

shows remnants of cementite nanowires encapsulated by CNTs, which prevents the wires from dissolving in acid.

The presence of CNTs in these swords is not surprising as it is now well known that CNTs can be produced from carbon at high temperature – the laser ablation and arc-discharge methods involve high temperature. The repeated heating and hammering (forging) results in band formation from segregation at a microscopic level of some impurity elements. It is quite probable that these elements may be responsible for the growth of CNTs, which in turn initiate formation of cementite nanowires and coarse cementite particles. Are the high mechanical strength and flexibility of Damascus blade due to the presence of CNTs? Further detailed studies may provide an answer to this question. However, even 400 years ago Indians were aware of the importance of *wootz* steel and Damascus swords, which are now proved to contain carbon nanostructures.

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