Carbon Nanotubes in Keeladi Potteries

Manivannan Kokarneswaran, Prakash Selvaraj, Thennarasan Ashokan, Suresh Perumal, Pathikumar Sellappan, Durai Murugan Kandhasamy, Nagaboopathy Mohan, Vijayanand Chandrasekaran

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Discovery of carbon nanotubes in Keeladi potteries

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Black coatings were observed in the inner side of pottery shreds obtained from Keeladi excavation. They were characterized by Raman spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. These studies revealed a presence of single-walled carbon nanotubes, multi-walled carbon nanotubes, and layered sheets in the coating. These nanomaterials were prepared in the 6th century BC and stable till now.

Synthesis and usage of nanomaterials are not only the outcomes of developments in modern science and technology. There are reports documented the usage of nanomaterials in the ancient arts and tools. It indicates that ancient days humans were aware of the uniqueness of these materials and the methods of synthesizing it. But might not know the scientific principles at the nanoscale and its unusual properties. For instance, the presence of Cu and Ag nanoparticles has been identified in glazed Islamic potteries1 and the Renaissance pottery from Mediterranean region2. These 0-D metal nanoparticles were used to improve the lustre of the potteries dates back to 8th - 9th century AD3. Reibold et al. observed the presence of 1-D nanomaterials such as multi-walled carbon nanotubes (MWCNT) in Damascus steel4. It was believed that the superior strength of the Damascus sabre has been attributed to the presence of carbon nanotubes (CNT). This was the first observation of CNTs in ancient objects which dates back to the 16th - 18th century. In this work, we present evidence for the presence of CNTs in black coatings given in the inner side of pottery’s shards that are excavated from Keeladi, Tamilnadu, India. Radiocarbon dating indicated the Keeladi settlement’s period to 6th - 3rd century BC5. To the author’s knowledge, the discovery of CNT in the Keeladi shards is the oldest among the nanostructure recognized till now from the ancient artefacts reported elsewhere in the world.

Pottery shards, metal pieces and fossil remnants are more common in all archaeological excavations. However, the uniqueness of Keeladi shards is the black coating which remained intact for more than two thousand years. The most interesting factor is its smoothness also not degraded much. Among the shards inspected, there are still some pieces retaining the smooth shiny surface intact. Since the coating is more than 2000 years old, unless it possesses robust mechanical and chemical stability to resist or isolate from the varying environmental conditions it becomes practically impossible to be stable till now. In order to understand the nature of the coating and its constituents, surface and elemental analysis have been carried out using Raman spectroscopy, Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

The Raman spectrum obtained from the black coating confirmed that it is indeed a carbon form as shown in Fig. 1. It reveals the presence of first-order Raman transition associated with the Defect band (D) and the graphite band (G) of carbon. The D and G band are entangled with fewer signatory peaks. The de-convoluted bands of each shoulder peak are shown in different color code attributing the presence of various components. The band observed at 1589 cm⁻¹ corresponds to in-plane vibration (E₂g mode) of the sp² bonded carbon generally indicated as G band. The de-convoluted D band observed at 1354 cm⁻¹, 1234 cm⁻¹, and 1473 cm⁻¹ are corresponds to the defects in the hexagonal graphitic carbon layer, commonly indicated as D₁, D₄, and D₅ band respectively6.
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Figure 1. Raman spectrum of the black coating showing the presence of D, G and 2D band. The Defect (D) band has been deconvoluted in to various components(D1, D4 and D5) as marked in different colors. The presence of D, G and 2D band confirms the presence of hexagonal graphitic carbon layer and sp² bonded carbon.

The broad absorption feature observed around 2600 cm⁻¹ is attributed to the second-order Raman transition commonly called as 2D band. The D and G peaks indicate that the black coating is indeed a carbonaceous in nature but not amorphous carbon. It may correspond to disorder graphite or defective graphene / graphene oxide or other carbon allotropes. The presence of sp² carbon domains measured from the high-resolution C1s x-ray photoelectron spectrum (Fig S2. in supplementary information) confirms the Raman findings.

To get insights on the nature of the carbon species observed in the Raman spectrum, TEM analysis was carried out to reveal its structure and morphology. Fig. 2(a) shows the presence of bundles of single-wall carbon nanotubes (SWCNT). The average tube diameter was found to be 0.6 ± 0.05 nm and the wall separation was 0.2 ± 0.01 nm. The variation in CNT diameter can be identified due to the bending and twisting effect. A close observation of the bundle confirms minuscule bending which might be the cause of fluctuation. It is interesting to note that the smallest theoretical limit for the diameter of CNT is 0.4 nm. Experimentally 0.3 nm was also observed but these small diameter nanotubes are seen as an innermost part of the MWCNT. For SWCNT, the smallest diameter reported was 0.43 nm. It is very surprising to observe SWCNT from an archaeological artifact with 0.6 ± 0.05 nm and has been stable for around 2600 years. Fig. 2(b) shows the MWCNT observed from the coating. The spacing between the walls was found to be as 0.34 nm which was in good agreement with the spacing between the (002) lattice plane of the graphite. Also, the inner diameter of the MWCNT is 3 ± 0.15 nm. Curling and damage seen in the tube was the reason for differences in inner diameter as reported in literatures. Our TEM analysis confirms the presence of CNTs in the black coating. Although it was not the only constituents, there were regions which revealed the presence of layered sheets, possibly graphene or graphene oxide as shown in Fig. 2(c).

It is interesting to know the presence of CNTs from the samples that date backs to 6th - 3rd century BC, particularly, given the kind of tools availed at those periods. From the modern synthesis route, we know that elements like Fe, Si and Al can act as a nucleation site for CNTs. The XPS spectra (Fig. S1 in the supplementary information) indicate the presence of Fe, Al, Si, etc. possibly in the form of their oxides. High resolution spectra of Fe (Fig. S3 in the supplementary information) indicates that it is present in both +2 and +3 oxidation state. At this moment, the source of carbon for the coating remains unknown. A most plausible explanation is, it might be from the vegetal source used during the manufacturing of potteries and the black coating. Iron observed in the sample might have originated from the vegetal source itself or the soil. So the more scientific possibility would be the plant-based material should have been carbonized, forming different carbon allotropes at high temperature achieved during the firing process of pottery. The presence of iron in the plant source and also the soil might have catalysed the carbon to form SWCNT and MWCNT. High temperature present in the firing process of pottery making might have favoured the formation of carbon nanotubes.

In general CNTs and Graphene are known for its superior mechanical strength than the bulk counterpart. The finding of these two carbon forms in the Keeladi coating raises the following
questions. (i) Does the ancient Keeladi settlement know the importance of these properties and adapted it intentionally? (ii) Given the black coating is observed in the inner portion of the shard, if these potteries were used for edible preparation or preservation then did they aware of the cytotoxic nature of CNT and Graphene sheets? In spite of other unanswered questions, it is interesting to see the strong footprints of 1D and 2D carbon-based nanomaterials used about 600 BC ago with diameter closer to theoretical limit and retained its stability.

Conflicts of interest

There are no conflicts to declare.

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Supporting information

Experimental methods
Raman measurement is performed in LABRAM-HR Confocal laser Micro-Raman spectrometer which employs Ar+ laser with wavelength 514.5 nm as a photon source. The sample was cleaned and the spectrum is recorded in room temperature. For TEM, the black coating powder was drop casted in carbon-free Pd and Cu holey grids and imaged using 200 keV. The image in Fig. 1 (a) and (b) are acquired with Cu holey grid using FEM-2100 Plus electron microscope and Fig. 1 (c) is acquired with 2-3 nm Pd coated grid using FEI Techani T20 electron microscope. To retain the original signature of the coating minimal sample preparation has been adapted to realize an electron transparent region. As a result, dark contrast was observed in the major portion of the grid indicating bulk nature. However, the electron transparent regions revealed interesting features such as randomly distributed SWCNT bundles and MWCNTs. The surface cleaned samples are used for measuring X-ray photoelectron spectrum using PHI VersaProbe III which employs Al Kα x-ray source.

Figure S1: XPS spectrum measured for the black coating showing the presence of various elements
Figure S2: De-convoluted high resolution C1s XPS spectrum of the black coating.
Figure S3: De-convoluted high resolution Fe 2p XPS spectrum of the black coating. The ratio of Fe 2p$_{3/2}$/Fe2p$_{1/2}$ is 1.97 which is very close to the theoretical estimate as 2.

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