



# High pressure studies on core/shell amorphous carbon nanostructures

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**Abstract.** High pressure behaviour of core/shell amorphous carbon (a-C) nanostructures was studied using synchrotron X-ray diffraction (XRD) and Raman spectroscopy up to  $\sim 25$  GPa. These nanostructures having spherical a-C shells with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles at the core were synthesized by catalyst-assisted lamp black method. The typical size of core ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)/shell (a-C) is  $\sim 5$  nm/20 nm. Comparative XRD of the core ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) in opened- and closed-shell (a-C) shows that the carbon shells do not fully transmit the applied high pressure inwards, under hydrostatic conditions. Raman spectroscopy shows that the graphitic G-mode blue shifts reversibly with applied pressure with a coefficient  $\sim 3.5$  cm<sup>-1</sup> GPa<sup>-1</sup>, which is  $\sim 25$  to 40% less than that for graphite and carbon nanotubes. It is suggested that a rigid and crosslinked structure of the carbon shell might be lossy for the observed pressure drop.

**Keywords.** Core/shell configuration; pressure damping; carbon nanostructures.

## 1. Introduction

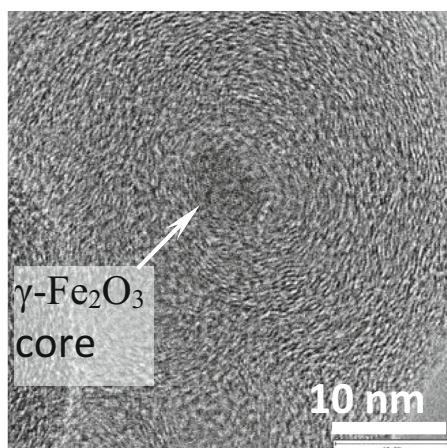
High pressure study on carbon by Mao *et al* [1] suggests a noticeable change in sp<sup>2</sup> to sp<sup>3</sup> hybridization around 16 GPa. Other representative studies [2–5] show that the high pressure response of carbon does not converge to a well-defined trajectory of hybridization, pressure value, relaxation time, etc. In this perspective, considering glassy carbon particles under mechanical loading alone, one report suggests a shear strength superior to that of diamond [6]. On the other hand, another report [7] presents a counterview based on reasonable model based on experiments. Further, it is not clear how the structural changes affect the transmission of pressure through carbon itself and can be attributed to lack of reasonable models compatible with experimental conditions at nanoscale.

In the present study, we attempt to estimate the pressure drop across a nanometric-sized amorphous carbon (a-C) nanoparticle by directly measuring pressure across its shell thickness. We use core ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)/shell (a-C) nanoparticles, wherein the core particles act as pressure marker in two configurations namely, (i) enclosed-in-shell and (ii) open-shell, thereby revealing the effect of carbon shell.

## 2. Experimental

### 2.1 Synthesis of materials

Core/shell nanoparticles were synthesized by catalytic lamp black method [8]. In brief, 0.2 molar solution of ferrocene (catalyst precursor) in olive oil (carbon precursor) was used for combustion synthesis. Core ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)/shell (a-C) nanoparticles were obtained, with typical spherical-shaped core/shell diameter of 5 nm/20 nm. Transmission electron microscopy reveals their typical structure, as shown in figure 1. Carbon shell is highly defective graphitic/amorphous carbon. The obtained powder was treated with diluted hydrochloric acid to get rid of the freestanding iron oxide particles, then washed with de-ionized water several times before drying in air at room temperature. Carbon shells were opened by radio frequency (rf) plasma treatment in order to obtain exposed  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (exposed core) particles for control experiment. The rf treatment caused change in colour of the specimen due to removal of carbon. Based on visual observations, a small amount of specimen at intermediate stage of shell removal was also extracted for high pressure observations.



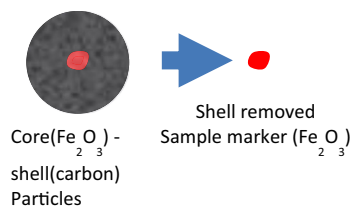
**Figure 1.** High-resolution transmission electron micrograph.

## 2.2 Definition of the problem and characterization

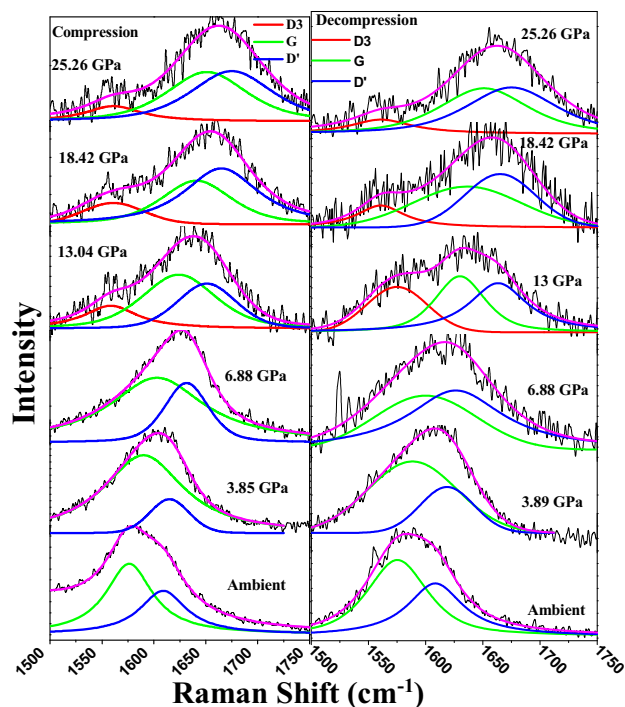
Core particles (pressure marker) under compression can be schematically represented, as in figure 2, in two configurations namely, (i) with a-C shell and (ii) without shell. Therefore, these will see the pressure experienced through the (i) finite a-C thickness and (ii) pressure transmission medium. Thus, the core particles are used as a pressure marker/sensor. Synchrotron-based X-ray diffraction (XRD;  $\lambda_{\text{photon}}$  0.633 Å) at BL-11, Indus-2, RRCAT was employed to probe the response of the marker. Raman spectroscopy ( $\lambda_{\text{ex}}$  514 nm DPS laser) was employed to probe the microscopic response of the a-C shell. Methanol:ethanol (4:1) was used as pressure transmission medium and Ag/ruby was used as pressure measurement standards in XRD/Raman experiments, respectively.

## 3. Results and discussion

The phases present in the synthesized nanostructures were identified as  $\gamma\text{-Fe}_2\text{O}_3$  and graphitic amorphous carbon, as established in [8]. High pressure Raman spectra of these core/shell particles are shown in figure 3 and the important results from high pressure XRD are summarized in table 1. These XRD results suggest a pressure drop across the C shell, as seen from the fact that more pressure is required to achieve the same  $d_{311}$  spacing of the core ( $\gamma\text{-Fe}_2\text{O}_3$ ) particles in core-shell configuration as compared to the exposed-



**Figure 2.** Schematic representation of with- and without-shell conformation for the pressure marker core particles of  $\gamma\text{-Fe}_2\text{O}_3$ .



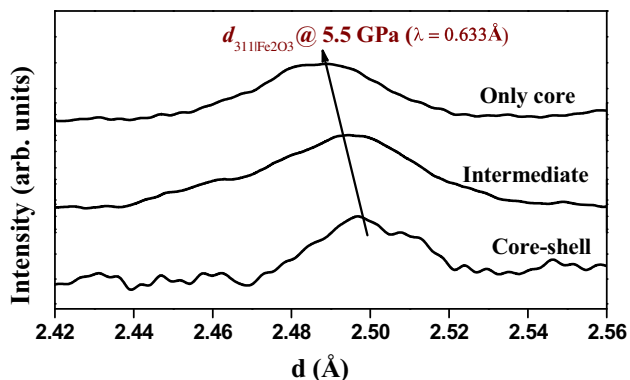
**Figure 3.** Raman spectroscopy of core/shell carbon particles with increasing (left) and decreasing (right) pressure. Continuous curves represent best fit.

core. A comparative representation of the core particle XRD peak  $d_{311}$  showing this trend from core (shell-fully intact)—core(shell-intermediate removal stage)—core(shell fully removed) is shown in figure 4. The effect of a-C shell on the pressure experienced by the core particle becomes evident from this figure. Apparent higher bulk modulus of the core ( $\gamma\text{-Fe}_2\text{O}_3$ ) particles too suggests the same. Thus, carbon shell thickness of the order of 10 nm as observed from transmission electron microscopy (figure 1) is responsible for a pressure drop of  $\sim 2.4$  GPa at the applied pressure of 5.6 GPa, meaning  $0.24$  GPa  $\text{nm}^{-1}$ . Pressure drop in shear conditions is reported earlier [6,7] but our values represent direct measurement across a thin slab of carbon.

We now proceed to comment on the possible mechanism of this huge pressure drop in amorphous carbon from Raman spectroscopy results. Analysis presented in detail in [9] of high pressure Raman results reveal the G-mode blue shifts reversibly with pressure with a coefficient of about  $3.79$  and  $3.45$   $\text{cm}^{-1}$   $\text{GPa}^{-1}$  for compression and decompression, respectively, and no structural phase transition was observed up to the maximum applied pressure of 25 GPa. These shifts are more than  $2.1$   $\text{cm}^{-1}$   $\text{GPa}^{-1}$  observed for glassy carbon [7] but more less than  $4.7$   $\text{cm}^{-1}$   $\text{GPa}^{-1}$  for graphite [10]. Appearance of Raman G-peak means the presence of  $\text{sp}^2$  domains of carbon, which are connected through their boundaries, defects and also  $\text{sp}^3$ -like clusters of carbon. It is long known that the carbon soot/carbon black is a mixture of  $\text{sp}^2$  and  $\text{sp}^3$ . From a recent electron energy loss spectroscopy and high-resolution transmission

**Table 1.** Pressure response of marker particles ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> core) in different configurations.

Pressure marker ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> core) configuration	Observed bulk modulus of core (GPa)	$d_{311}$ spacing of $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> core particle (Å)	Applied pressure for observed $d_{311}$ (GPa)
Core/shell	253.6 ± 5.6	2.498	5.4
Core exposed to pressure transmission medium	184.3 ± 3.2	2.498	2.8



**Figure 4.** XRD patterns of iron oxide (only core, top curve) and carbon shell-encapsulated iron oxide (undamaged core/shell, bottom curve) samples at the pressure of around  $\sim 5.5$  GPa, while the middle curve is the pressure response of intermediate specimen that is with incomplete shell removal. The peak corresponds to (311) reflection of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The iron oxide without shell is having less d-spacing as compared to the iron oxide that is inside the carbon shell around the applied pressure of  $\sim 5.5$  GPa, which indicates the lesser compression of later one. The trend is self-evident.

electron microscopy based study, it is clear that the  $sp^2$  fraction in their studied typical carbon soot is around 84–96% [11]. We can then suppose that the minor  $sp^3$  carbon atoms should occupy the grain boundaries of majority  $sp^2$  domains and behave like dangling bonds or in other words part of certain defects and cause strain within the  $sp^2$  grains if occupying space within a grain. This may arguably present greatest hurdle for geometrical conformation between two  $sp^2$  domains even if they are in direct atomic contact. This is also clear from a previous study, which shows based on mainly XRD analysis of amorphous carbon under pressure that the strain increases upon application of pressure and the structure reverts back but particle size does not change [12]. Based on these facts from previous studies, we present a simplistic model that can be visualized as interconnected network of this milieu, as represented schematically in figure 5. Such a structure may provide a lot of sites where the non-conforming bonds are bent rather than compressed. It may be noted that while the  $sp^3$  tetrahedral coordination is rigid in long-range crystalline order, single or few atomic  $sp^3$  clusters may be susceptible for distortion. This would result in absorbing



**Figure 5.** Schematic representation of crosslinked  $sp^2$  and  $sp^3$  carbon clusters, while the orientation mismatch presents geometrical hurdle for compressive forces though bending might be preferred.

some effect of pressure rather than transmitting to the crystalline domain, where the actual compression effects can be seen, thereby evidently hardened Raman modes of crystalline domains.

#### 4. Conclusion

Our study suggests the presence of rigid structure of amorphous carbon nanoparticles as compared to graphite. High pressure XRD and Raman results indicate that geometrically non-conforming crosslinks of  $sp^2$  and  $sp^3$  carbons in the amorphous carbon structure might act as a lossy framework, causing the pressure drop observed in XRD.

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