

Raman Spectroscopy for The Determination of Relative Crystallinity of Carbon Fibers[†]

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Abstract

Analogous to X-ray diffraction technique, the light scattering technique discovered by Sir CV Raman has great potential in quantifying the crystallinity of new materials, like the highly crystalline pitch based carbon fibers (NX90 and NX100). For comparison the Raman spectra of polyacrylonitrile (PAN) based carbon fibers (T700SC) were also recorded. From the Raman spectral analysis, it was found that the pitch based carbon fibers exhibit far far higher degree of crystallinity compared to PAN based carbon fibers. In fact, PAN based fibers have carbon micro structure analogous to the amorphous activated carbon with the regular disorder band (D band) and the graphitic band (G band). In sharp contrast to the PAN based carbon fibers, the pitch based fibers showed polycrystalline graphitic structure. In the Raman spectra of the pitch based carbon fibers, the signal at $\sim 1348 - 1358 \text{ cm}^{-1}$ should not be mistaken with the regular disordered carbon structure found in amorphous carbon materials and this band should not be attributed to the regular D band. Rather, this band located in the range of $\sim 1348 - 1358 \text{ cm}^{-1}$ corresponds to the crystalline graphitic structure that arise due to the well crystallized graphite with smaller crystallite size ($\sim 29 \text{ nm}$). As the D band itself is absent in the pitch based fibers, the conventional Raman intensity ratio ($R = I_D/I_G$), corresponding to the degree of graphitization or degree of crystallization, cannot be used as a measure. Rather, a revised Raman intensity ratio, given by, $R_{\frac{NX90}{NX100}} = \frac{(I_{CG}+I_G)_{NX90}}{(I_{CG}+I_G)_{NX100}}$, where CG ($\sim 1348 - 1358 \text{ cm}^{-1}$) and G ($1575 - 1584 \text{ cm}^{-1}$) corresponds to crystalline graphite and graphite respectively, provides an accurate quantitative measure of the relative crystallinity of highly crystalline materials like NX90 and NX100 where the disordered structure is almost absent. Using the revised Raman intensity ratio, it was found that the degree of crystallinity of NX90 is 2.3 times higher than that of NX100. Thus Raman spectroscopy forms a quantitative analytical tool for evaluating the relative crystallinity of carbon fibers.

Keywords: Carbon fibers, crystallinity, graphitization, Raman spectroscopy, Revised Raman intensity ratio, pitch, polyacrylonitrile

INTRODUCTION

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Ever since Sir Chandrasekhara Venkata Raman and his student KS Krishnan have first reported on the new type of secondary radiation (modified light scattering) from sixty different dust-free common liquid samples that were carefully prepared by distillation, there was an intense interest in the discovery. The new type of secondary radiation was subsequently named as Raman scattering and the phenomena was known as Raman effect that received the Nobel prize for Physics in the year 1930 [1]. Subsequently, the phenomena of Raman effect was exploited as a finger print technique for the structural characterization and identification of

chemical species and the technique was known globally as Raman spectroscopy.

Raman spectroscopy is the ultimate analytical tool for distinguishing crystalline materials from amorphous materials, and it is more so in the specific case of carbon materials. A web of science crossing the keywords, namely, “Raman spectroscopy and crystallinity”, showed only 5629 results (as on 14th September 2024) indicating that the analytical technique is under-utilized. The consistent growth of the research area on the use of Raman spectroscopy for characterizing the crystallinity of materials during the past decade is shown in Figure 1.

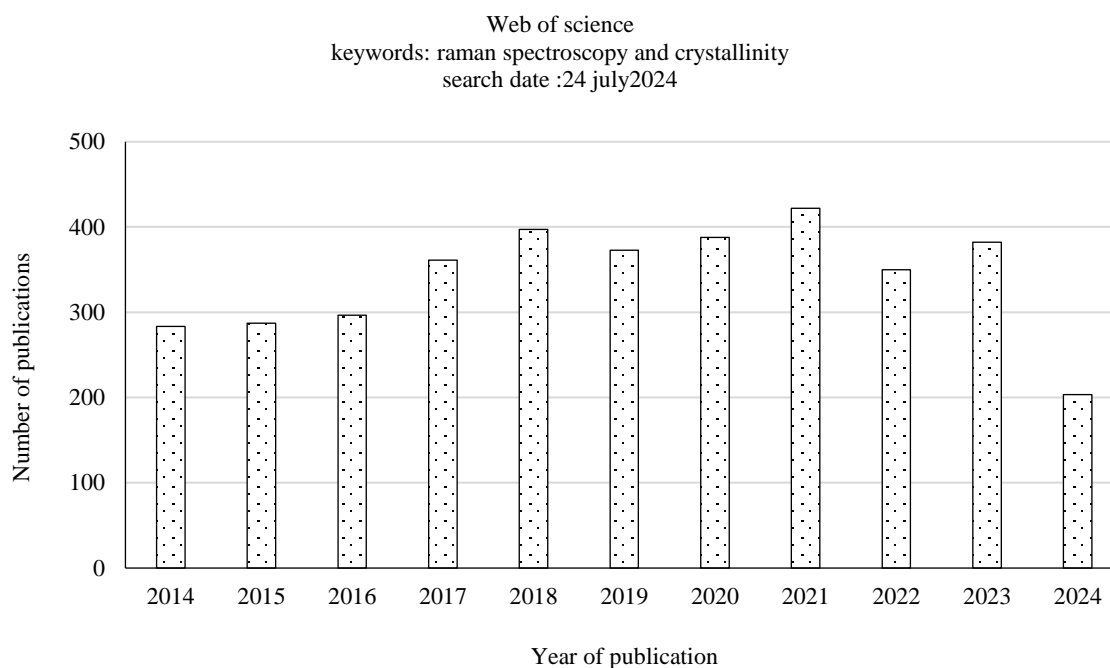


Figure 1. Consistent growth of the research on the application of Raman spectroscopy for the evaluation of the crystallinity of materials. (2014-2024)

Use of Raman spectroscopy for the crystalline and microstructural characterization of carbon fibers is upcoming owing to the commercial use of these materials for strategic applications [2-5]. Carbon fiber reinforced plastics (CFRPs) are the materials of the future with applications in almost all realms of human activity, namely, aeronautics, astronautics, aquanautics and geonautics [6]. Carbon fibers (CFs) with the unique properties like the high specific strength, light weight, high surface polarity act as the main load bearing component of the CFRPs. necessitating the structural characterization of carbon fibers. Typical chemical structure of the feedstock pitch and the carbon fibers produced from pitch (NX 90 and NX100) were shown in Figure 2. Likewise the chemical structure of the PAN and the carbon fibers produced from PAN were shown in Figure 3

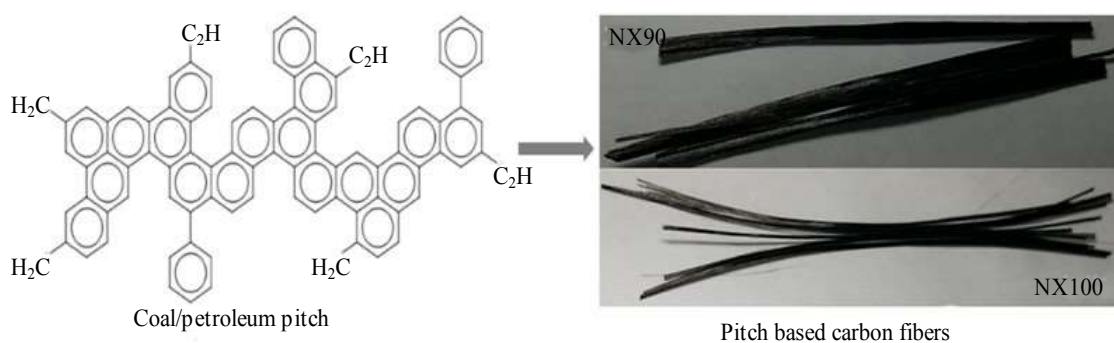


Figure 2. Chemical structure of coal/petroleum pitch and the photograph of the pitch based commercial sized carbon fibers (NX90 and NX100).

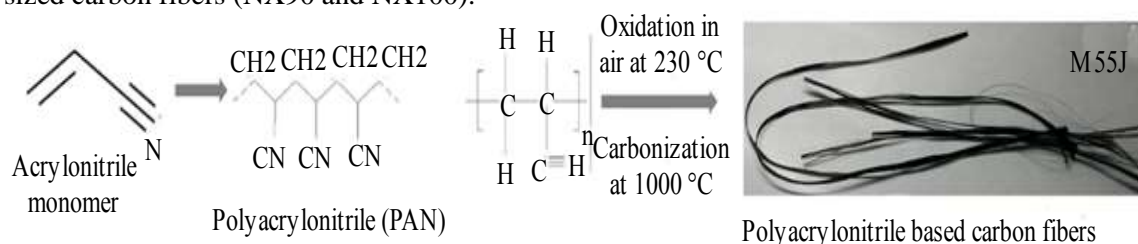


Figure 3. Process for the production of polyacrylonitrile (PAN) based carbon fibers, M55J.

Raman spectroscopy was found to be a potential analytical technique in understanding the relative crystallinity of carbon fibers based on the feedstock as well as the preparation method of the carbon fibers. The current research article is focused on the study of the relative crystallinity of pitch (NX90 and NX100) derived and polyacrylonitrile derived carbon fibers (T700SC-24K series) using Raman spectroscopy.

Experimental

PAN based sized carbon fibers (T700SC-24K series) were provided by Toray industries Inc., Pitch based carbon fibers (NX90 and NX100) were procured from Nippon graphite fiber Co., Samples of carbon fibers (NX90, NX100 and T700SC) for Raman analysis were prepared adopting the same procedure reported elsewhere [7]. Raman spectra of the pitch based (NX90, NX100) and polyacrylonitrile (PAN) based (T700SC) carbon fibers were recorded on Senterra R200-L dispersive Raman microscope (Bruker optics, GER).

RESULTS AND DISCUSSION

Degree of Crystallization (Graphitization) of Carbon Fibers Using Raman

Microstructural characterization of carbon materials by Raman spectroscopy is well documented [8-11]. Raman spectra of pitch based (NX90 and NX100) and PAN based (T700SC) carbon fibers are shown in Figures. 4-6. For comparison an overlay diagram of the Raman spectra of carbon fibers NX90, NX100 and T700SC were shown in Figure 7. Striking difference in the crystallinity is observed between the pitch based and PAN based carbon fibers. In the case of pitch based fibers (NX90 and NX100) both first order ($1200\text{-}1650\text{ cm}^{-1}$) and second order Raman lines ($2400\text{-}3300\text{ cm}^{-1}$) are observed. Such a pattern with sharp intense peaks at $\sim 1584\text{-}1619\text{ cm}^{-1}$, $\sim 2701\text{-}2690\text{ cm}^{-1}$ accompanied with a third Raman signal at $\sim 1348\text{-}1358\text{ cm}^{-1}$ but with lower intensity is characteristic of polycrystalline graphitic carbon [10]. For comparison, Raman spectral features of various amorphous and graphitic carbon materials are shown in Figure 8. The signal at $\sim 1348\text{ cm}^{-1}$ in the case of NX90 and at 1358 cm^{-1} in the case of NX100 should not be mistaken to the usual D band attributable to disordered carbon materials that appears, nearly in the same range ($1348\text{-}1376\text{ cm}^{-1}$). Rather, in the specific instance of NX90 and NX100, the peak at $\sim 1348\text{-}1358\text{ cm}^{-1}$ is connected to the two other signals corresponding to polycrystalline graphitic structure, namely the first order Raman line at $\sim 1584\text{-}1619\text{ cm}^{-1}$ and the second order Raman line at $\sim 2701\text{-}2690\text{ cm}^{-1}$. The signal at $\sim 1348\text{-}1358\text{ cm}^{-1}$ observed in the Raman spectra of NX90 (Fig. 4) and NX100 (Figure 5) is attributed to the well crystallized graphite with smaller crystallite size ($\sim 29\text{ nm}$) [7]. In sharp contrast to the Raman spectral pattern of pitch based fibers, the PAN based fibers (T700SC) showed the pattern typical of amorphous activated carbon with two first order Raman lines at 1376 cm^{-1} and 1596 cm^{-1} attributable to the disordered (D band) and graphitic (G band) carbon structures respectively present in T700SC (Figure 6). No second order Raman lines are seen in the Raman spectrum of T700SC. The first order Raman lines indicate only the structural order or disorder within the carbon sheet or layer, i.e., carbon plane along crystallographic a-axis [11]. First order Raman lines carry no information on the stacking order or disorder along the crystallographic

c-axis. Here, the term “graphitic” represents carbon atoms that are three coordinated and are bound by sp^2 type bonding orbitals. The term “graphitic” has nothing to do with the stacking of layer along the crystallographic c-direction [Figure 9].

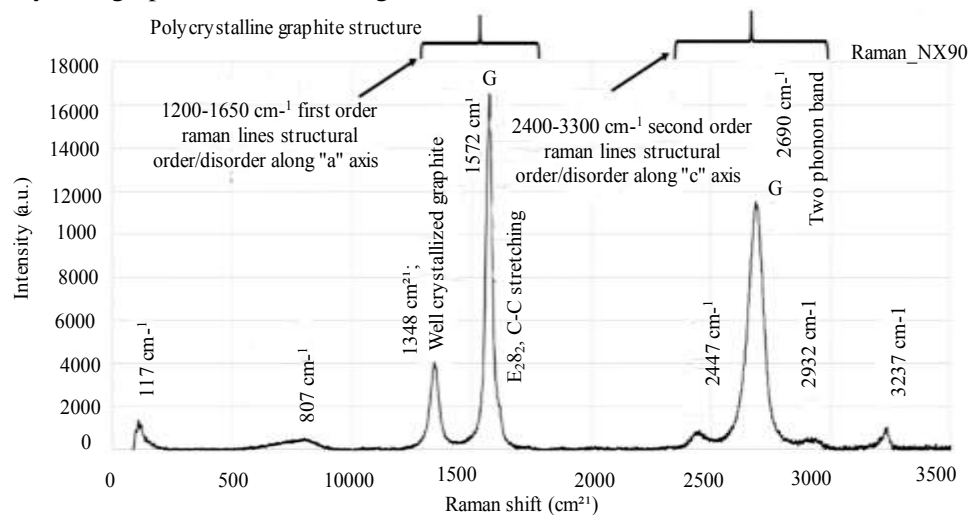


Figure 4. Raman spectrum of pitch based carbon fiber, NX90.

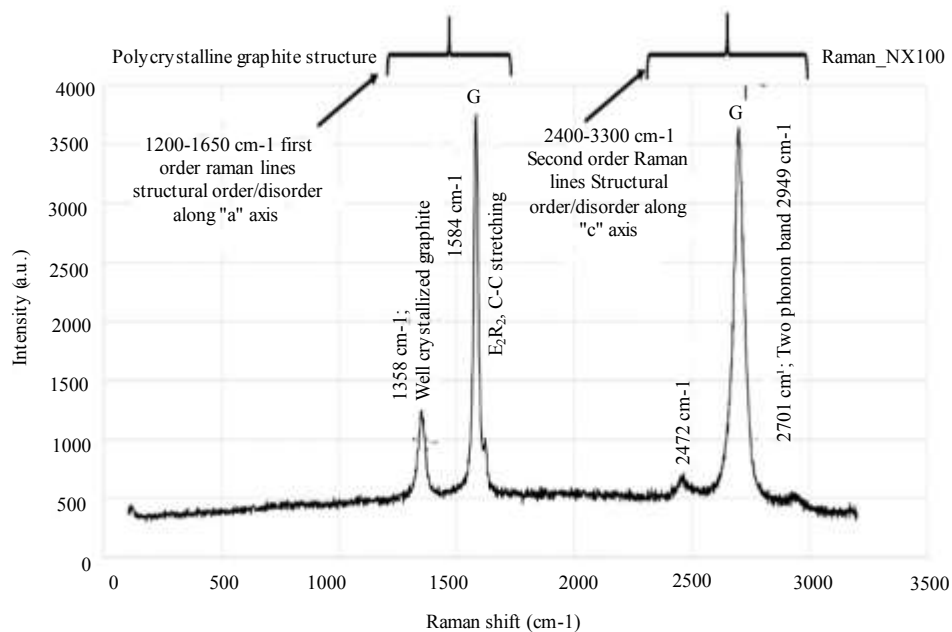


Figure 5. Raman spectrum of pitch based carbon fiber, NX100.

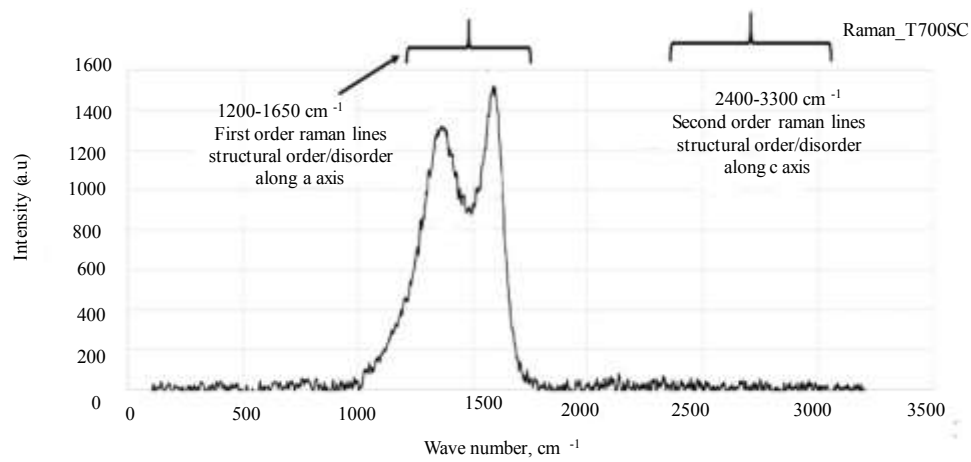


Figure 6. Raman spectrum of polyacrylonitrile (PAN) based carbon fiber, T700SC.

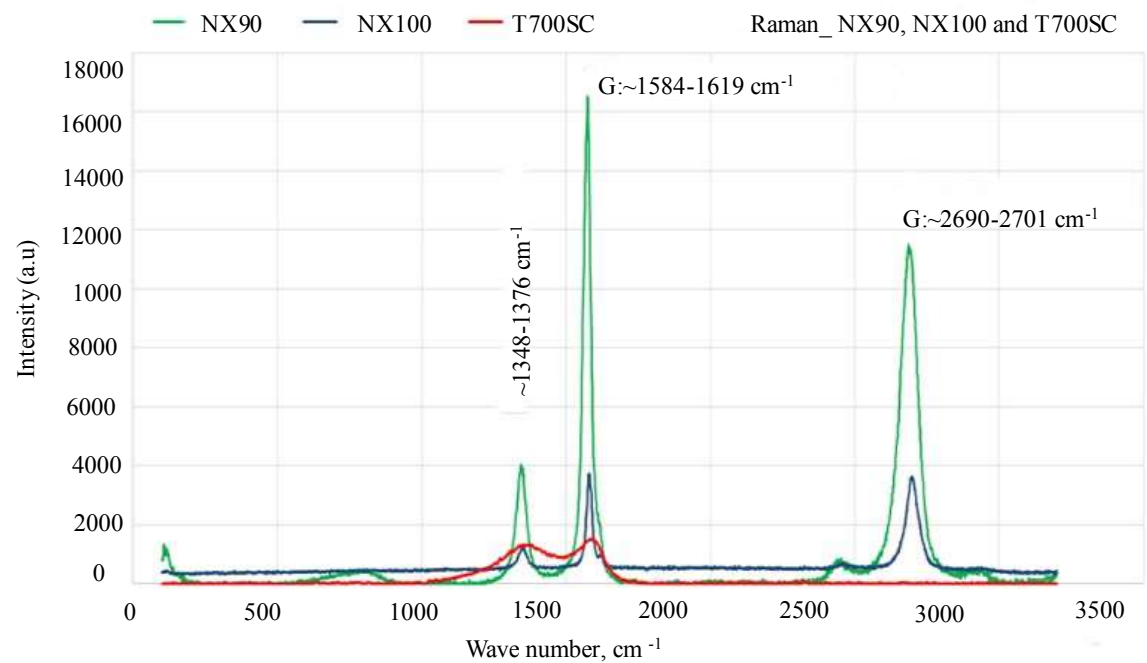


Figure 7. Raman spectra of pitch based carbon fibers (NX90, NX100), and polyacrylonitrile (PAN) based carbon fiber, T700SC – a comparison.

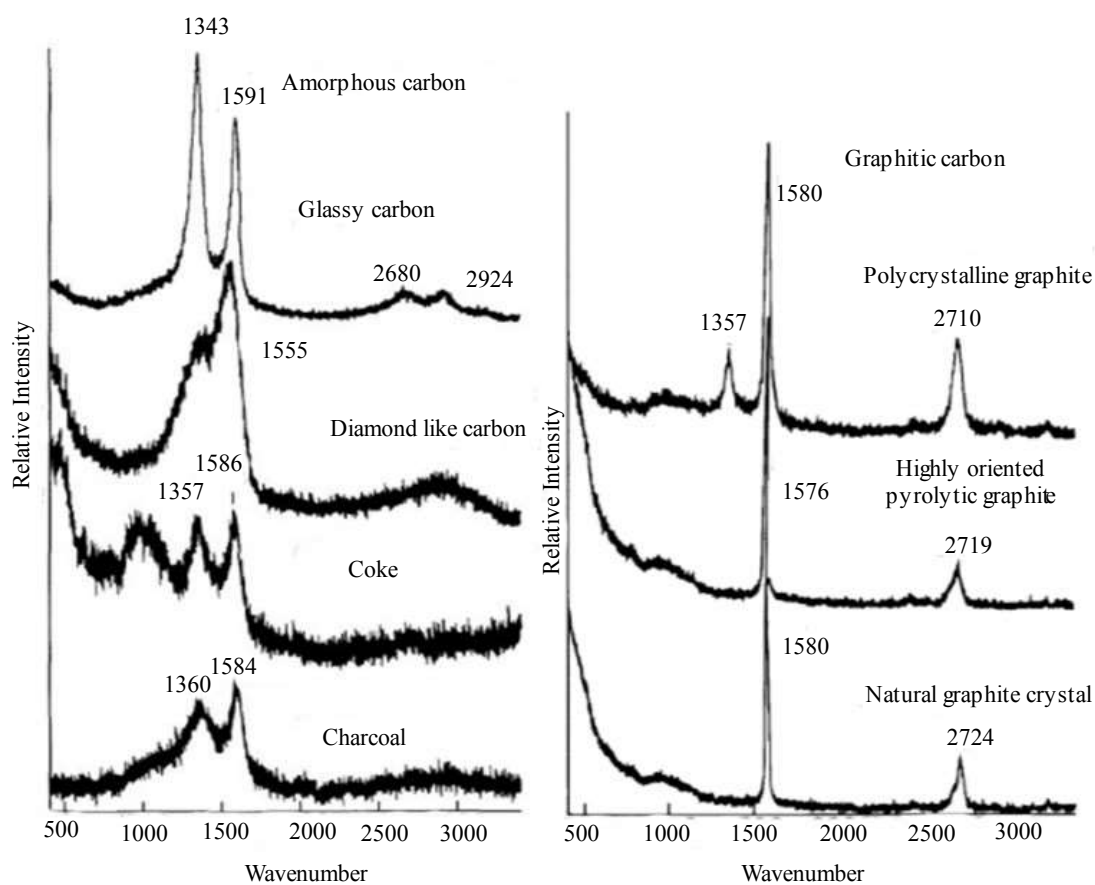


Figure 8. Examples of Raman spectral pattern of amorphous and graphitic carbon materials – a comparison [10].

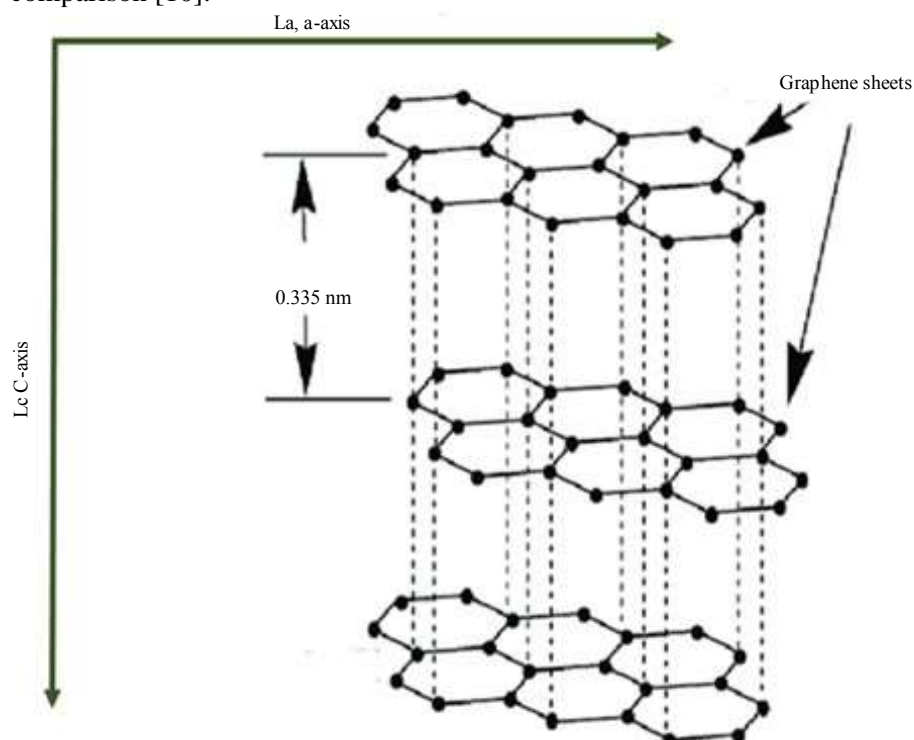


Figure 9. Alignment of graphene sheets made up of hexagonal rings of carbon atoms along the a-axis and the c-axis [7].

Raman intensity ratio (I_D/I_G), the ratio of the first order Raman line at $\sim 1348\text{-}1376\text{ cm}^{-1}$ (D band) to the intensity of the signal at $\sim 1596\text{-}1619\text{ cm}^{-1}$ is a measure of the degree of graphitization of carbon materials. The evaluation of degree of graphitization in the case of PAN based fibers is easy, as the D band and G band are present, which are typical of any other amorphous activated carbon materials. As a result, a simple ratio of area under the peaks corresponding to D and G bands gives the Raman intensity ratio (R) which is a measure of the degree of graphitization. Lower, the value of (R), higher is the degree of graphitization of the carbon material. As shown in Table 1, the Raman intensity ratio for the PAN based carbon fibers T700SC is 1.5834. This value is well with-in the range of the degree of graphitization of well-known amorphous activated carbon materials that exhibit a value in the range of 1.4 to 1.9 [8, 9, 12]. In contrast, the corresponding value for pitch based fibers is zero as the band corresponding to disordered amorphous carbon is absent in the polycrystalline graphitic NX90 and NX100. However, such a comparison of degree of crystallinity is quite complicated in the case of pitch based carbon fibers, namely, NX90 and NX100, as the D band corresponding to disordered carbon itself is absent in these carbon materials owing to their polycrystalline graphitic structure and an exceptionally high degree of graphitization. A new measure is essential to compare the extent of graphitization in these materials, as using the regular Raman intensity ratio will lead to a value of degree of graphitization only to zero for both NX90 and NX100 (Table 1). Thus no appreciable comparison of the degree of graphitization is possible by using the regular measure of the Raman intensity ratio proposed in literature.

Table 1. Degree of crystallinity of carbon fibers from Raman intensity ratio ($R=I_D/I_G$)

Carbon fiber	Peak intensity frequency, ν (cm^{-1})*		Raman intensity ratio, $R=I_D/I_G$
	D band	G band	
NX-90, Pitch	(D band absent)#	1575 (683682)	0
NX-100, Pitch	(D band absent)#	1584 (237507)	0
T700SC, PAN	1371 (319031)	1596 (201489)	1.5834

* Values in the parenthesis show the peak intensity
#D band is absent in the case of NX90 and NX100

However, a revised Raman intensity ratio, as shown in equation (1), can be used as a measure to compare the relative degree of graphitization between different carbon materials with exceptionally high degree of graphitization, as in the case of pitch based carbon fibers.

$$R_{\frac{NX90}{NX100}} = \frac{(I_{CG}+I_G)_{NX90}}{(I_{CG}+I_G)_{NX100}} \quad (1)$$

Where R_r , is the revised Raman intensity ratio

I_{CG} , is the intensity of the Raman line corresponding to the crystallized graphite (CG band) at $\sim 1348\text{-}1358\text{ cm}^{-1}$

I_G , is the intensity of the Raman line corresponding to the graphitic carbon (G band) at $\sim 1584\text{-}1596\text{ cm}^{-1}$

Table 2. Degree of crystallinity of pitch based carbon fibers with polycrystalline graphitic structure from revised Raman intensity ratio, $R_{\frac{NX90}{NX100}} = \frac{(I_{CG}+I_G)_{NX90}}{(I_{CG}+I_G)_{NX100}}$

Carbon fiber	Peak intensity frequency, ν (cm^{-1})		Raman intensity ratio (revised), $R_{\frac{NX90}{NX100}} = \frac{(I_{CG}+I_G)_{NX90}}{(I_{CG}+I_G)_{NX100}}$
	CG band	G band	
NX-90, Pitch	1348 (227737)	1575 (683682)	2.3
NX-100, Pitch	1352 (158879)	1584 (237507)	

*CG-Crystallized graphite

Use of such a revised Raman ratio, leads to reliable conclusion that the degree of graphitization of NX90 is 2.3 times higher than of NX100 (Table 2). Direct comparison of the degree of pitch based and

PAN based carbon fibers is not valid as both have different microstructural features. Clearly, PAN based fibers exhibit much lower degree of graphitization.

CONCLUSION

With the first-ever report by Sir CV Raman on the new type of secondary radiation called the Raman scattering by over sixty dust free common liquids carefully prepared by distillation using very high intense solar radiation as the light source, there has been a break through that lead to a powerful spectroscopic technique called Raman spectroscopy for the finger print detection of chemical species. The Raman intensity ratio ($R=I_D/I_G$), namely, the ratio of intensity of the signal arising from the disordered carbon to that of the intensity of the signal arising from the graphitic carbon is a measure of the degree of graphitization or degree of crystallinity. Lower the value of R, higher will be the degree of crystallization. Such a ratio is applicable for most of the crystalline materials with disordered (D) and graphitic (G) bands in the first order Raman lines. However, there are some special cases, as those observed in highly crystalline materials like the carbon fibers from the pitch, where no D band is observed, and rather a peak due to the crystallized graphitic structure is observed in the usual location of the disordered carbon structure, which is often mistaken to be due to the disordered carbon structure, in addition to the regular G band at a higher frequency value. In such cases, a different measure, namely, revised Raman ratio need to be adopted to get an accurate value of the relative degree of crystallinity of any two highly crystalline materials, like NX90 and NX100, as in the present case. The new concept of the revised Raman intensity ratio is elaborated with its usefulness in the specific instances where in the D band is absent. Using such a measure, it was found that the NX90 is 2.3 times more crystalline than NX100. Such a comparison of degree of crystallinity helps to choose the best material for producing carbon fiber reinforced plastic (CFRP) materials for high end applications, including space exploration, where light weight and structural stability are the determining features.

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†Dedicated to the legendary polymer Chemist Professor Xinling Wang, SJTU, on the occasion of the Chinese teacher's day on 10th September 2024.

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