PRAMANA
— journal of
physics

Vol. 71, No. 5
November 2008
pp. 971–977

Morphology of carbon nanotubes prepared via chemical vapour deposition technique using acetylene: A small angle neutron scattering investigation

D SEN[1,*], K DASGUPTA[2], J BAHADUR[1], S MAZUMDER[1] and D SATHIYAMOORTHY[2]
[1]Solid State Physics; [2]Powder Metallurgy Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[*]Corresponding author. E-mail: debasis@barc.gov.in

Abstract. Small angle neutron scattering (SANS) has been utilized to study the morphology of the multi-walled carbon nanotubes prepared by chemical vapour deposition of acetylene. The effects of various synthesis parameters like temperature, catalyst concentration and catalyst support on the size distribution of the nanotubes are investigated. Distribution of nanotube radii in two length scales has been observed. The number density of the smaller diameter tubes was found more in number compared to the bigger one for all the cases studied. No prominent scaling of the structure factor was observed for the different synthesis conditions.

Keywords. Small angle neutron scattering; carbon nanotube; chemical vapour deposition.

PACS Nos 61.05.fg; 61.48.De

1. Introduction

In 1991, Ijiama created a landmark by imaging CNT for the first time. So research on CNTs is still in the teenage years. A CNT can be envisioned as a graphite sheet rolled into a seamless cylinder. Single walled nanotube (SWCNT) consists of cylinder with only single wall while multi-walled nanotubes (MWCNT) comprise an array of concentrically nested rings like the rings in the trunk of a tree. Synthesis of CNTs can be achieved by various methods that involve the catalytic decomposition of a carbon containing gas or solid. Some of the common techniques are, the chemical vapour deposition (CVD), arc-discharge, laser vaporization, etc. However, it has been shown [1] that the synthesis conditions like temperature, carrier gas, pressure etc., catalyst type and carbon sources have influence on the structure and the properties of the resulting CNTs.

Table 1. Parameters and their levels for the preparation of the CNTs by CVD.

Sample	Catalyst	Catalyst conc. (%)	Temperature (°C)	Catalyst support
CNT-1	Ni-formate	5	700	Magnesia
CNT-2	Ni-formate	10	600	Alumina
CNT-3	Ni-formate	15	800	Carbon black
CNT-4	Co-formate	5	600	Carbon black
CNT-5	Co-formate	10	800	Magnesia
CNT-6	Ferrocene	5	800	Alumina
CNT-7	Ferrocene	10	700	Carbon black
CNT-8	Ferrocene	15	600	Magnesia

SANS and SAXS are well-established non-destructive techniques for the characterization of the mesoscopic structures in materials [2,3]. Here we present the SANS/SAXS investigations on MWCNTs prepared by CVD.

2. Experimental

In the present studies our objective was to synthesize CNTs from acetylene. Four parameters have been varied in different levels. These are synthesis temperature, type of catalyst, concentration of catalyst and type of catalyst-support material (table 1).

SANS experiments were performed using a double crystal-based medium resolution SANS facility at the Guide Tube Laboratory of Dhruva reactor, Trombay, India [4]. SAXS data were measured using the rotating anode (Rigaku)-based SAXS instrument, BARC, Mumbai, India.

Measured SANS/SAXS profiles have been corrected for background transmission and instrument resolution and are shown in figure 1 (normalized to unity at the lowest q value).

3. Data analysis and discussions

It is seen that the SANS profile for each specimen can be broadly categorized into two zones, one below (Zone-I) and the other above $q \sim 0.045$ nm^{-1} (Zone-II). The higher q part of Zone-I follows a power-law behaviour q^{-n1}, where $n1 \leq 3$. For Zone-II, there exists a slight bump/bending at around $q = 0.12$ nm^{-1}. At this stage, at least qualitatively, these observations indicate the presence of two length scales in the system. As the contour length of the CNTs is quite large compared to the radius (typically in few hundreds of micrometer to millimeter and is significantly out of instrumental resolution), the two length scales corresponding to Zone-I and Zone-II reflect the scattering from the cross-sections of the CNTS with radius distributions significantly separated. In order to verify the same, scanning electron microscopy

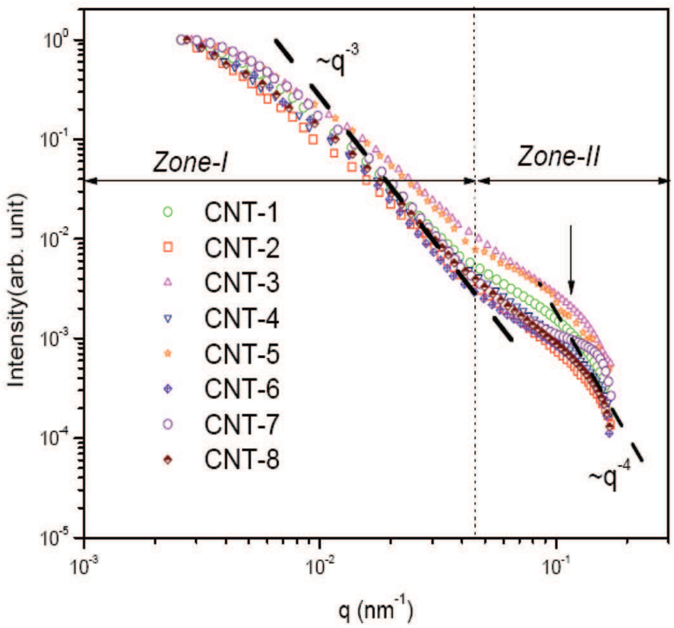

Figure 1. SANS data in log–log scale.

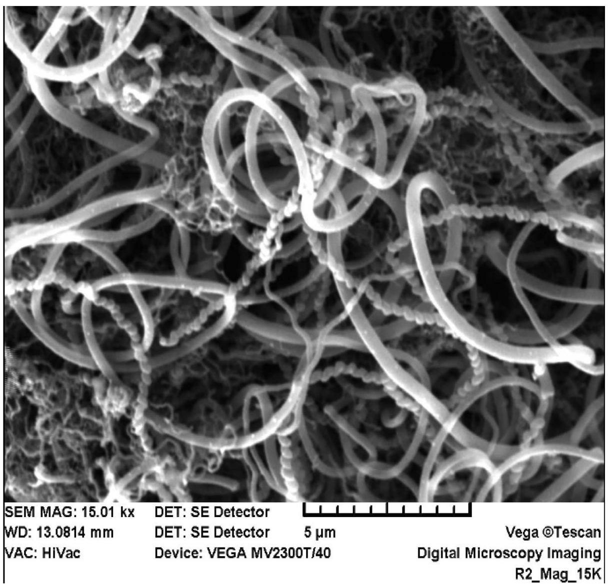

Figure 2. SEM micrograph of CNT-2.

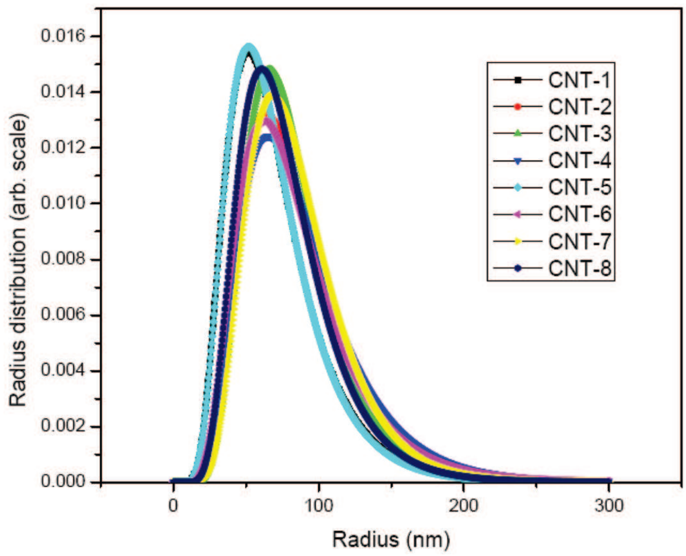

Figure 3. Distribution of the bigger tubes.

(SEM) was performed on the specimens. It is revealed from the SEM micrograph (figure 2) that the CNTs are mainly of two types namely, one with bigger and the other with smaller cross-section. Further, the tubes are not long rigid cylinders rather they are flexible cylinders. Qualitatively, it is also observed that the number density of the tubes with smaller radius is somewhat higher than that of the higher radius tubes. Initially, the SANS profiles have been analysed in the light of the cylinder cross-section scattering model with polydispersity in radial direction. For two distributions, total intensity can be written as

$$I(q) = \frac{C_1}{q}\int P(q)V(r)^2 D_1(r)\mathrm{d}r + \frac{C_2}{q}\int P(q)V(r)^2 D_2(r)\mathrm{d}r. \tag{1}$$

($P(q)$ is the form factor for the cross-section of a cylinder with radius r. $V(r)$ is the volume of the tube with radius r. $D(r)\mathrm{d}r$ is the probability of finding a tube with radius r.)

C_2/C_1 represents the ratio of the number density of the smaller to bigger tubes (in the present case C_2 corresponds to smaller size distribution and C_1 corresponds to bigger size distribution). It is again emphasized that both the terms in the above equation are necessary for the simultaneous fit of data both in Zone-1 and Zone-2. The estimated distributions are depicted in figures 3 and 4. The ratio of C_2/C_1 for the CNT-1 to CNT-8 samples are found to be 295, 294, 702, 520, 498, 409, 583 and 288 respectively. This shows that the number density of the smaller diameter tube is more than that of the bigger diameter tube.

SANS data were also analysed using flexible cylinder model [5,6]. Kuhn length (twice the segment length) for the bigger CNTs were found to be beyond the instrument resolution and hence not mentioned in table 2.

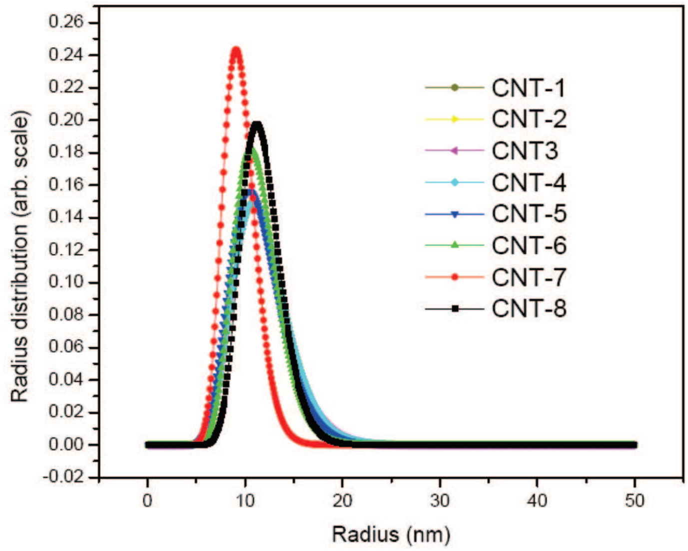

Figure 4. Distribution of the smaller tubes.

Table 2. Parameters from flexible cylinder model.

Sample	R_{C_1} (nm)	R_{C_2} (nm)	Kuhn length$_{C_1}$ (nm)
CNT-1	124	16	378
CNT-2	124	14	176
CNT-3	116	16	261
CNT-4	126	14	176
CNT-5	131	15	241
CNT-6	122	15	377
CNT-7	128	15	455
CNT-8	128	15	336

Having obtained a quantitative measure of the cylinder morphology, it is pertinent to ask whether for the different processing conditions the CNTs, in a statistical sense, posses any scaling of the structures.

For the present case the inverse of the first moment (q_1) of q over the SANS profile has been taken as a measure of the characteristic length scale. It is seen from figure 5 that although there is some overlapping of the scaled structure factors $\left(F(q/q_1) = \frac{q_1^3 I(q)}{\sum q^2 I(q)\delta q}\right)$ for q/q_1 up to 3, the same does not hold good for the higher values of q/q_1. This implies that although the higher length scale structures posses some kind of self-similarity, the same breaks down for the lower length scale structures. The specific surface area may be obtained from the scattering profile if the high enough q range is accessed where the Porod behaviour (variation of scattering intensity as $\sim q^{-4}$) is observed. In order to do so, SAXS experiment on CNT-1 sample has been carried out for a q range 0.08–2.3 nm^{-1}. The combined

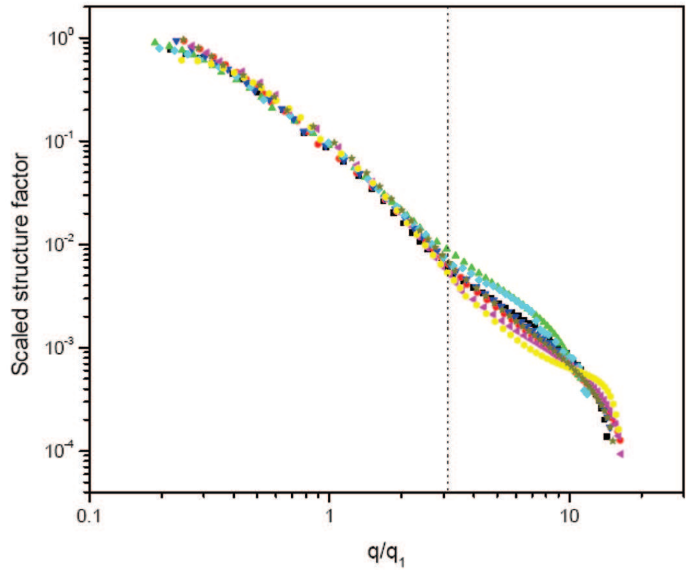

Figure 5. Scale structure factors.

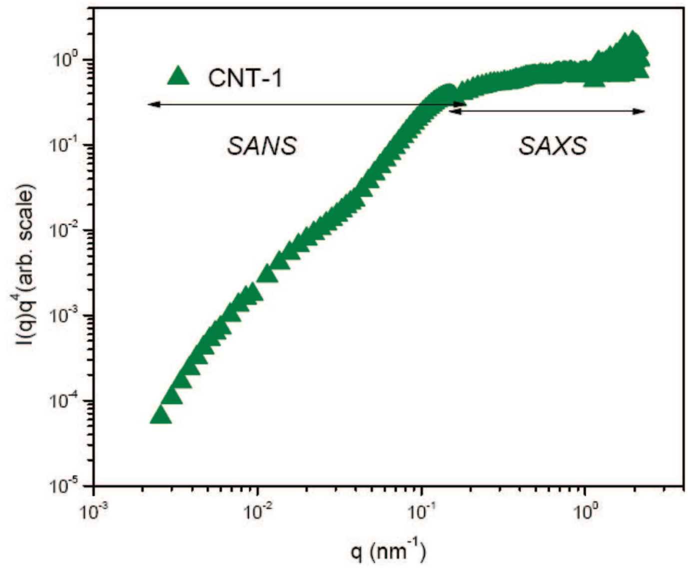

Figure 6. Combined SANS/SAXS data.

SANS–SAXS data (spanning a q range of 0.003–2.3 nm^{-1}) is shown in figure 6 in Porod representation. It is seen that the profile reaches nearly a plateau at $q \sim 0.55$ nm^{-1}. (In the overlapping region, the shape of the SANS and SAXS profiles was found almost identical and SAXS and SANS data have been normalized in this region but SAXS data are shown only beyond the SANS data (>0.173 nm^{-1}).) The specific surface area was calculated to be 269 m^2/g.

4. Conclusions

It is shown that although the source of carbon remains unchanged in all cases, the variation in synthesis parameters has a significant effect on CNT morphology and their number density. It is also revealed that SANS is an effective tool to characterize the radial distribution, specific surface area of CNT. Further, it also gives a measure of the scaling behaviour of structures in a statistical sense for various synthesis conditions of CNT. As the hydrogen storage property of CNTs is closely associated with its radial distribution, the present study can throw light to construct a correspondence between the hydrogen storage capacity and the cylinder morphology. Our next step will be to explore this possibility.

Acknowledgements

The authors would like to thank Dr P U Sastry for the SAXS experiments.

References

[1] K Dasgupta, R Venugopalan, G K Dey and D Sathyamoorthy, *J. Nanoparticle Res.* (2007); doi:-10.1007/s 11051-007-9219-5
[2] S Mazumder, D Sen, A K Patra, S A Khadilker, R M Cursetji, R Loidl, M Baron and H Rauch, *Phys. Rev. Lett.* **93**, 255704 (2004)
[3] D Sen, O Spalla, O Tache, P Haltebourg and A Thill, *Langmuir* **23**, 4296 (2007)
[4] S Mazumder, D Sen, T Saravanan and P R Vijayaraghavan, *J. Neutron. Res.* **9**, 39 (2001)
[5] J S Pedersen and P Schrutenberger, *Macromolecules* **29**, 7602 (1996)
[6] W R Chen, P D Butler and L J Magid, *Langmuir* **22**, 6539 (2006)