

## Better Dispersability of Un-Functionalized Multiwalled Carbon Nanotubes Through Sonication Techniques

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Different sonication techniques have been applied to increase dispersion efficiency of carbon nanotubes. During sonication (probe and bath), the effects of good dispersion on un-functionalized multiwalled carbon nanotubes (MWCNTs) and microstructure structure were characterized by tunneling electron microscopy (TEM) and Raman spectroscopy. The particle size distribution of the dispersed multiwalled carbon nanotubes was determined by using dynamic light scattering (DLS). The estimated length and diameter was observed to be *ca.* 210 and 9.44 nm (bath sonication) and *ca.* 396 and 10.04 nm (probe sonication) from the TEM images.

**Key Words:** Multiwalled carbon nanotube, Dispersion, Sonication, Dynamic light scattering.

### INTRODUCTION

Carbon nanotubes (CNTs) have attracted considerable attention since past several years because of their prospects in basic science and potential in many technological applications due to their extraordinary properties *i.e.*, mechanical, electrical and thermal<sup>1,2</sup>. However, even after a decade of research, the full potential of employing carbon nanotubes as reinforcements has been limited because of the difficulties associated with dispersion of entangled carbon nanotube during processing and poor interfacial interaction between carbon nanotubes and polymer matrix. The nature of dispersion problem for carbon nanotubes is rather different from other conventional fillers, such as spherical particles and carbon fibres, because carbon nanotubes are characteristic of small diameter in nanometer scale with high aspect ratio (> 1000) and thus extremely, large surface area. In additions, the commercialized carbon nanotubes are supplied in the form of heavily entangled bundles, resulting in inherent difficulties in dispersion. For the effective use of carbon nanotube an excellent distribution and dispersion is an essential precondition. The purity and functional groups on the surface of the carbon nanotubes as well as mainly their entanglements and strength of agglomerates influence the dispersibility of carbon nanotubes in different media. Ultra-sonication of carbon nanotubes dispersions is a common tool used to break up the carbon nanotubes agglomerates in solution based processing techniques. Ultrasonic can

be done by different ways: using either an ultrasonic bath or an ultrasonic probe into the solvent. The ultrasonic probe oscillates at a fixed frequency and produces a conical field of high energy in the fluid. The solvent within this conical field undergoes nucleated boiling and bubble collapse that is primary mechanism by which ultrasonic energy disperses particles<sup>3</sup>. This may help to de-bundle nanotubes by providing high local shear particularly to the nanotubes ends. In present study, we have compared two different sonication techniques (probe and bath) for good dispersions of un-functionalized multiwalled carbon nanotubes (MWCNTs) in dimethyl formamide (DMF). During sonication, the effects of good dispersion/sonication on multiwalled carbon nanotubes are characterized by tunneling electron microscopy (TEM), Raman spectroscopy and dynamic light scattering (DLS).

### EXPERIMENTAL

Commercially available multiwalled carbon nanotubes (MWCNTS) and dimethyl formamide (DMF) were used. 0.5 Wt % of multiwalled carbon nanotubes was immersed in DMF solution and sonicated *via* two different approaches (probe and bath). One sample was sonicated through a bath sonicator (ultrasonic cleaner bath Model CT-408) for a period of 12 h at room temperature at 42 kHz. Under similar conditions, another sample was sonicated with probe sonicator for 10 min (1 min on and 1 min off) to avoid the breaking of sample tube due to overheating effect. The principal of this techniques is that when

an ultrasound propagates *via* a series of compression, attenuated waves are induced in the molecules of the medium through it passes. The production of these shock waves promotes the "peeling off" of individual tubes located at the outer part of nanotube bundles or agglomerates and thus results in the separation of individual tubes from the bundles<sup>4</sup>. The transmission electron microscope Hitachi (H-7500) 120 KV is equipped with CCD cameras were used to study the surface morphology and dispersity of the multiwalled carbon nanotubes. The Raman spectrum was investigated with a Renishaw *in via* Raman microscope with an argon ion laser at an excitation wavelength of 514.5 nm. The particle size distribution was measured by dynamic light scattering (DLS, Zetasizer Nano ZS (Malvern instrument UK) quipped a monochromatic coherent 4mW Helium Neon laser ( $\lambda = 633$  nm) as light source. All measurements were performed in disposable cuvettes. The z average hydrodynamic particle diameter is obtained from the cumulant analysis of the normalized electric field autocorrelation function (ACF). It is calculated by the Stokes-Einstein equation with diffusion coefficient determined by the decay time of autocorrelation function (ACF).

$$d(H) = \frac{KT}{3\pi} \eta D$$

where  $d(H)$  = hydrodynamic diameter,  $D$  = translation diffusion coefficient,  $K$  = Boltzmann's constant,  $T$  = absolute temperature,  $\eta$  = viscosity.

The diameter that is measured in dynamic light scattering (DLS) is a value that refers to how a particle diffuses within a fluid so it is referred to as a hydrodynamic diameter. The diameter that is obtained by this technique is the diameter of a sphere that has the same translation diffusion coefficient as the particle. The translation diffusion coefficient will depend not only on the size of the particle "Core" but also on any surface structure, as well as the concentration and type of the ions in the medium. From cumulant analysis it is possible to get the z-average hydrodynamic diameter of the particles and polydispersity index. The PDI is a parameter that defines the particle size distribution of the nanoparticles (in particular the width of the distribution) as obtained from the photon correlation spectroscopy (PCS) analysis (Malvern Instrument Ltd. UK). PDI is defined as dimensionless measure of the broadness of the size distribution. The system reports a PDI values lies between 0 and 1, in which a PDI value of 0.1 will represent monodispersity and greater than 0.1 means polydispersity in the sample with values in the range 0.1-0.25 indicating a narrow size particle distribution<sup>5,6</sup>. Dynamic light scattering provides information for length distribution whereas zeta potential which provides the information for the degree of dispersion. The length of the tube closely related to degree of the dispersion.

## RESULTS AND DISCUSSION

In present study on colloidal suspensions of unfunctionalized multiwalled carbon nanotubes (MWCNTs) in dimethyl formamide (DMF), different sonication techniques (bath and probe) was employed to first aid to mixing and forming a homogeneous dispersion. The amounts of colloidal suspension of multiwalled carbon nanotubes in dimethyl

formamide (DMF) were visualized with bath and probe sonicator as shown in Fig. 1. It is clear from visualization that the resulting colloidal suspension was jet black under bath as well as probe sonication. It was also observed that the initial sonication treatment quickly form large aggregates and settled at the bottom of the bottle under probe sonication, but no sedimentation was observed in bath sonication within three months sitting at room temperature. The colloidal suspension stability in aqueous solution was also studied by visual inspection over time.

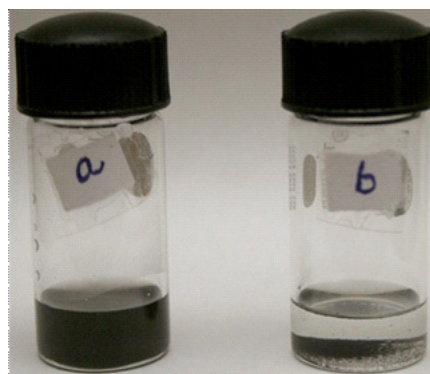


Fig. 1. Multiwalled carbon nanotube in DMF dispersion in (a) bath sonication (b) probe sonication

The tunneling electron microscopy (TEM) images of the colloidal suspension of multiwalled carbon nanotubes (MWCNTs) in DMF solution followed by probe and bath sonication, showed the presence of multiwalled carbon nanotubes with average diameter of 10.07 nm and estimated length ranging from *ca.* 257-973 nm in case of probe sonication, whereas in bath sonication having average diameter 9.44 nm, estimated length ranging from *ca.* 210-427 nm as shown in Fig. 2a and b. It is observed that multiwalled carbon nanotubes in the dispersion with bath sonication maintained the formation of long tube structure even after their some chopping induced by ultrasonic, but the trend was not similar with probe sonication, they are bundled and cut into shorter segments. TEM images revealed that no significant damage overall took place in multiwalled carbon nanotubes during probe sonicator. It was also observed that multiwalled carbon nanotubes cut into shorter segments and found irregular structure with with probe sonication. From these figures, multiwalled carbon nanotubes retained their external average diameter of 10-15 nm and estimated length to be *ca.* 210 nm (bath sonication) and *ca.* 396 nm (probe sonication).

The thin film of multiwalled carbon nanotubes directly deposited on Si-wafer at 60 °C for 15 min for the characterization of Raman spectra study. It is revealed from the Raman spectrum that the confirmation of multiwalled carbon nanotubes under bath and probe sonication. In case of probe sonication, the peak observed at 1589  $\text{cm}^{-1}$  (G-band) which is slightly shifted than bath sonication at 1581  $\text{cm}^{-1}$ . The samples are highly luminance so that the peaks observed was not so clear under bath sonication techniques shown in Fig. 3. It may be due to luminescence interference which is dependent on the dispersion of carbon nanotubes in the solution sample<sup>7</sup>. The peak at 1350  $\text{cm}^{-1}$  could be assigned to the vibration of the

carbon atom with dangling bonds in the plane terminations of disordered graphite<sup>8</sup> in both cases. The  $I_D/I_G$  ratio was 0.8591 probe sonication and 0.849 nm for bath sonication.

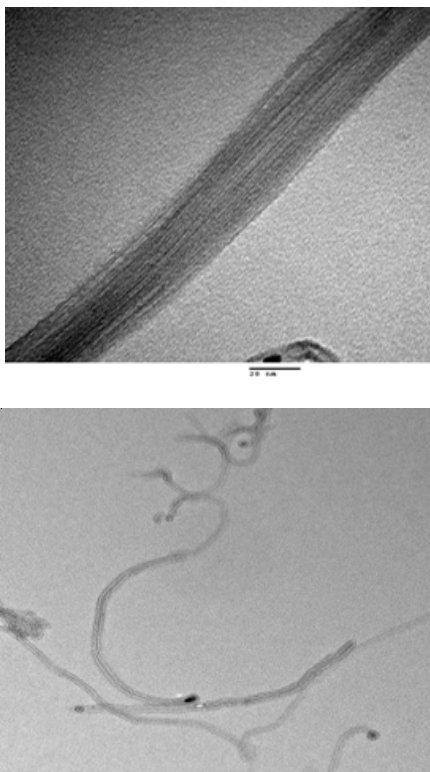


Fig. 2. (a) Multiwalled carbon nanotubes in DMF with bath sonicator

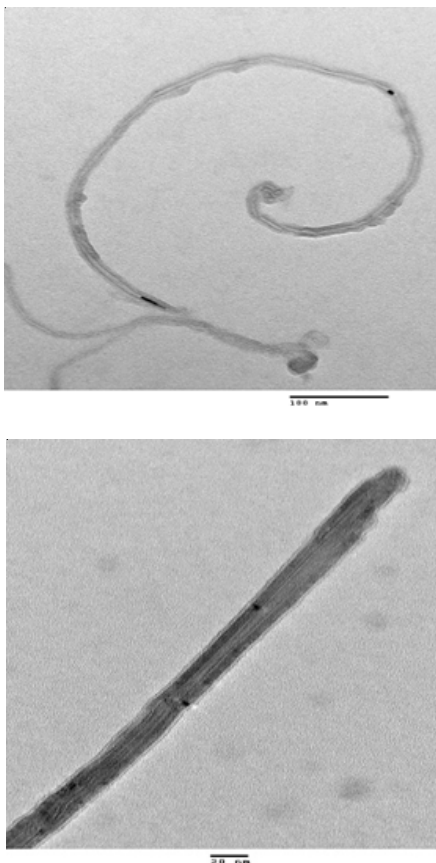


Fig. 2. (b) Multiwalled carbon nanotubes in DMF with probe sonicator

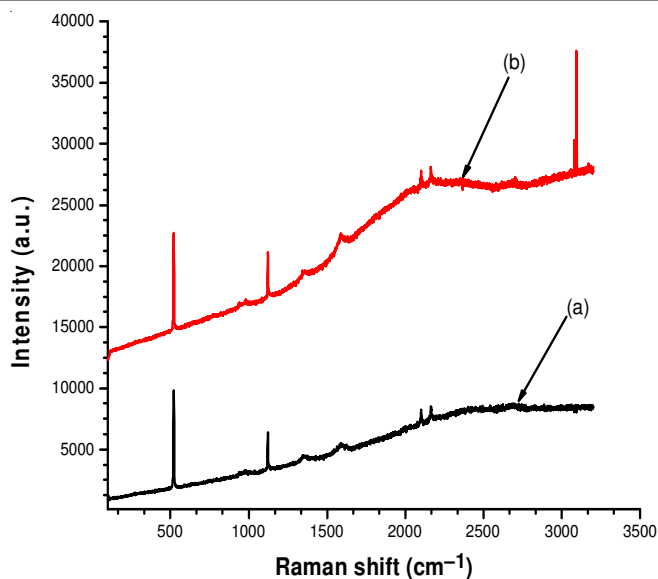


Fig. 3. Raman spectra of multiwalled carbon nanotubes immersed in DMF as deposited on Si-wafer (a) bath sonicator (b) probe sonicator

Fig. 4 shows the light scattering intensity distribution as a function of particle size. The effect of ultra sonication on multiwalled carbon nanotubes (MWCNTs) particle sizes evaluated by the DLS measurement for the hydrodynamic diameter which was numerically derived from the optical measurement of the Brownian motion of the target particles, on the assumption that the particles were spherical. The z-average hydrodynamic particle diameter from DLS is dependence on the ultrasonic techniques. The value of intensity weighted particle size distribution using bath sonication is generally lower compared to the intensity weighted value obtained by probe sonication. Thus it can be assumed that the ultrasonic treated agglomerates are not spherical. The particle diameters determined using DLS for both sonication techniques (bath and probe) shows big difference. The value varies between 1322 nm (probe sonication) and 165.9 nm (bath sonication). It is evident that the particle sizes in bath sonication appear smaller than probe sonication. It may be due to ultrasonic treatment or else. Especially in dispersions treated for a short ultrasonic time in DLS measurements bimodal and very broad distribution were found (probe sonication) indicating a heterogeneous particle distribution. With bath sonication treatment time the dispersions got more homogeneous and size distribution narrowed<sup>9</sup>. Sonication techniques effect the size distribution of multiwalled carbon nanotubes as demonstrated by the high polydispersity index (PDI) recorded for the samples confirmed from the DLS study. The PDI obtained by DLS was found to be higher (1.000) for probe sonication indicating heterogeneous particles and agglomerates existent in the dispersion. For bath sonication a polydispersity index of 0.373 was found and indicating the agglomerates is more homogeneous in size. In addition to this, the zeta potential values lies in the range from 0 to  $\pm 5$  showed the rapid coagulation or flocculation behaviour of the colloidal suspension of multiwalled carbon nanotubes (MWCNTs) under probe sonication (-2.80) but in case of bath sonication shows incipient (-6.50) stability.

TABLE-1  
PROPERTIES OF MWCNTS UNDERBATH AND PROBE SONICATION

Techniques	Z-Average (dnm)	PDI	Zeta potential (mV)	Zeta deviation (mV)	Conductivity (mS/cm)
Sonicator probe	1322 nm	1.000	-2.80	6.70	0.040
Ultrasonic cleaner bath	165.9 nm	0.373	-6.50	16.9	0.023

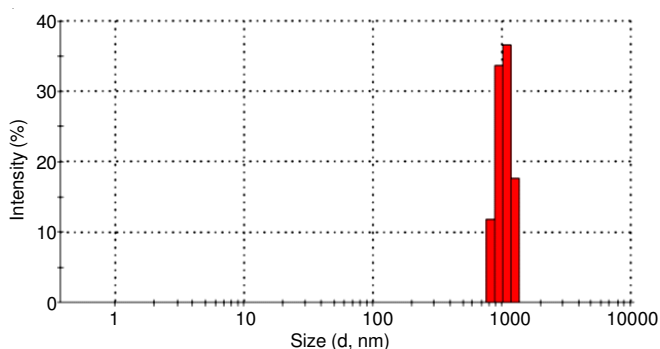


Fig. 4. (a) Size distribution Vs intensity of multiwalled carbon nanotubes in DMF with probe sonication

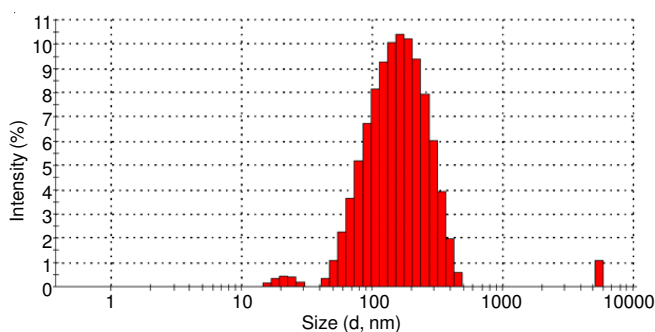


Fig. 4. (b) Size distribution Vs intensity of multiwalled carbon nanotubes in DMF with bath sonication

The greater the negative charge on the surface, the more negative is the value of the zeta potential. Decreasing the zeta potential of a particle could cause it to agglomerate even more since there is not as strong a repelling force between the particles as before. Short periods of sonication 10-12 min seem to have impact on the zeta potential as seen with colloidal suspension of multiwalled carbon nanotubes. It has been concluded that the bath sonication may effects the surface charge of the particle and the state of dispersion. The probe sonication can not significantly reduce agglomeration nor provide stable suspension of particles<sup>10</sup>. In Table-1; we have tabulated the corresponding average diameter, zeta deviation and conductivity for both techniques of our samples. The results showed that samples under both techniques were highly stable, indicated

by their negative values of zeta potential. The average zeta deviation was observed higher in case of bath sonication as compared with probe sonication but the conductivity behaviour is opposite.

### Conclusion

It is concluded from initial sonication treatment, quickly forms aggregates and settled at the bottom of the bottle under probe sonication, no sedimentation was observed within three months sitting at room temperature in bath sonication. Raman spectrum and TEM confirmation of multiwalled carbon nanotubes and calculated the diameter and estimated length which close to actual values. From DLS study, the particle size distribution is narrow and more negative value of zeta potential confirmed the more homogeneous and highly stable multiwalled carbon nanotubes in case of bath sonication as compared to probe sonication.

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### REFERENCES

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. J.H. Sung, H.S. Kim, H.J. Jin, H.J. Choi and I.J. Chin, *Macromolecules*, **37**, 9899 (2004).
3. L. Vaisman, H.D. Wagner and G. Marom, *Adv. Colloid. Interf. Sci.*, **128**, 37 (2006).
4. P.-C. Ma, N.A. Siddiqui, G. Marom and J.-K. Kim, *Composites: A*, **41**, 1345 (2010).
5. S. Kumar, T.D. Sang, F.E. Arnold, A.R. Battacharaya, B.G. Min, X.F. Zhang, R.A. Vaia, C. Park, W.W. Adams, R.H. Hauge, R.E. Smalley, S. Ramesh and P.A. Willis, *Macromolecules*, **35**, 9039 (2002).
6. J. Hilding, E.A. Grulke, Z.G. Zhang, F. Lockwood, *J. Dispers. Sci. Technol.*, **24**, 1 (2003).
7. C. Klinke, R. Kurt, J.M. Bonard and K.J. Kern, *Phys. Chem. B*, **106**, 11191 (2002).
8. C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng and M.S. Dresselhaus, *Science*, **286**, 1127 (1999).
9. B. White, S. Banerjee, S. O'Brien, N.J. Turro and I.P. Herman, *J. Phys. Chem. C*, **111**, 13684 (2007).
10. B. Krause, M. Mende, P. Potschke and G. Petzold, *Carbon*, **48**, 2746 (2010).