Improvement in Dispersion of SWCNT by Functionalization

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Abstract

This paper presents a study of dispersion of non-functionalized and functionalized Single Walled Carbon Nanotubes (SWCNT). Ethanol was used as solvent. The SWCNT suspensions were prepared by ultrasonication. The functionalization of SWCNTs was done by acid treatment. The purity of SWCNTs was analyzed using Energy Dispersive X-ray spectroscopy (EDX) of prepared SWCNT film.

Keywords: Single walled Carbon Nanotubes, EDX, Functionalization, and Dispersion.

Introduction

The carbon nanotubes (CNT) were discovered by Iijima in 1991 [1]. Since, then much attention was given to the extensive study of CNTs and their applications. Carbon nanotubes are rolled sheet of graphene with C-C bond length 1.42 Å. These are characterized by its chiral vector indices (n, m) which describe the properties of carbon nanotubes. The chiral vector of Carbon Nanotubes is given as $C_h = na_1 + ma_2$, where n and m are indices, a_1 and a_2 are unit cell vectors of hexagonal lattice. The diameter of CNT is given by

$$d = \frac{a}{\pi}\sqrt{n^2 + mn + m^2}$$

where a is equal to 0.142 nm. The chiral angle θ is the angle between chiral vector and zig-zag direction and is given by

$$\theta = \tan^{-1}\left(m\sqrt{3}\right)/(m + 2n)$$

In recent years, there has been a significant progress in the field of carbon nanotubes. But pristine CNTs have less dispersion ability in organic solvents because of bundles formation [2]. Hence it is difficult to disperse and align in the polymer matrix. This problem of dispersion and solubilization can be addressed by functionalization of CNTs. In addition to that, it enables further modification for applications [3, 4].

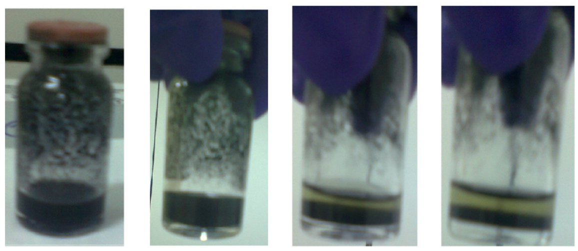
One of functionalization methods is the acid treatment [5]. By this treatment, the caps at the end of the SWCNTs are cut and ends get oxidized [6]. The addition of carboxyl functional group was observed during heat treatment in different acids with different concentration [7].

Experimental details

The SWCNTs used in this study were procured from Nanoshel-Intelligent Materials Pvt. Ltd. (synthesized by arc discharge method). It contains more than 80% SWCNTs with 0.7-2 nm diameter range, 5% of amorphous carbon and less than 5% residue. Nitric acid of concentration (69%) from Merck was used as received.

For functionalization of SWCNT, 40mg of SWCNTs were added to 50ml of nitric acid. The suspension was heated to 120^{0}C for 2 hours. The suspension was cooled down to room temperature and diluted with 250 ml DI water. The SWCNTs in the suspension was allowed to precipitate and decanted supernatant and added 250 ml of water. This process was repeated till suspension pH = 7 achieved. Then the SWCNTs were dried and added to ethanol and sonicated for 10 minutes to prepare suspension.

For Scanning Electron Microscopy (SEM) analysis, few drops of CNT suspension was coated on gold coated silicon wafer by drop casting. It was dried overnight at 90 ^{0}C.



(a) (b) (c) (d)

Fig. 1: Dispersion of SWCNTs (a) after sonication (b) 2 min (c) 5 min (d) 10 min

Results and discussion

As-received SWCNTs were dispersed in ethanol by using ultrasonicator. Fig. 1 shows that the dispersion of SWCNT in ethanol is poor. SWCNTs precipitation starts after 2 minutes and completely precipitates after 10 minutes.

After acid treatment functionalized SWCNTs were sonicated in ethanol. The dispersion of functionalized SWCNTs was analyzed at different intervals of time. Fig. 2 indicates that the functionalized SWCNTs were in dispersion for more time. Precipitation of functionalized SWCNTs started after 3 hours. From the Fig. 1 and Fig. 2 it can be concluded that the solubility of SWCNTs was increased after functionalization.

(a) (b) (c) (d) (e)

Fig. 2: Dispersion of SWCNTs after functionalization (a)after sonication (b) 10 min (c) 20 min (d) 30 min (e) 3 hour

The main reason for the increase of solubility was the attachment of –COOH functional group to SWCNT. With the functionalization, not only the solubility increases, but also opens possibility of attachment of other functional groups such as –COCl, -$CONH(CH_2)_{17}CH_3$.

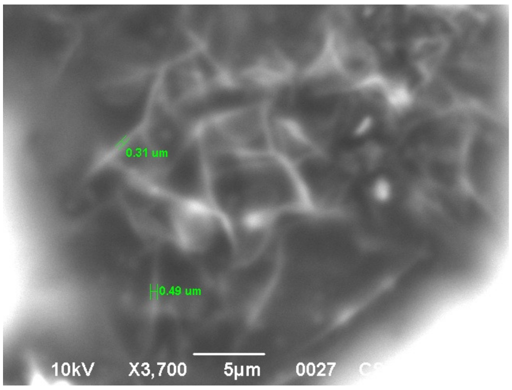


Fig. 3 (a): SEM image of SWCNT film prepared by drop casting method.

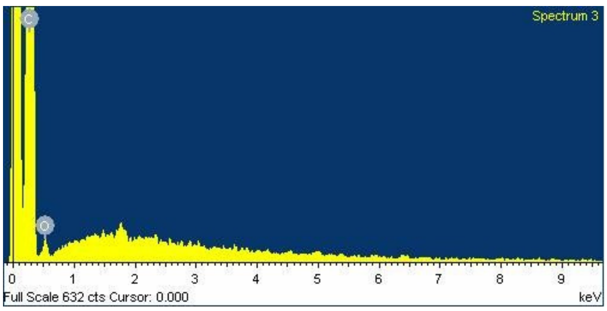


Fig. 3 (b): EDX spectrum of SWCNT film

Fig.3 (a) shows the SEM image of SWCNT film and typical SWCNT bundle sizes were 310 nm and 490 nm. Even though the bundles were small, they were not resolved by our SEM. Fig.3 (b) shows the EDX analysis. The EDX spectrum indicates that there were no metal particles in the CNTs and only 2.63 wt % oxygen was present which came from adsorption of oxygen by CNTs. Carbon was 97.32 wt%. The SWCNTs are 100% pure with respect to metallic impurities, which can be clearly observed from the EDX analysis.

Conclusion

The purity of as-received SWCNTs was analyzed with EDX. The poor dispersion ability of as-received SWCNTs in ethanol was observed. The acid treatment of SWCNTs was done which adds –COOH functional group to SWCNTs. The increase of dispersion ability of SWCNTs in ethanol was observed. This study will help for further processing of carbon nanotubes and for adding other functional groups, which can helps for gas sensing applications of SWCNT.

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