To Study the Role of Chemical Modification in Dispersion of Multi- Walled Carbon Nanotubes

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ABSTRACT: *Because of strong Vander Waal force, carbon nanotubes tend to aggregate into bundle that limits its applications in various fields. Homogenous dispersion of carbon nanotubes is an important issue. This paper reports the effect of chemical functionalization of multiwalled carbon nanotubes (MWCNTs) by introducing polar groups such as carboxyl groups in order to get better dispersibility in aqueous medium. Functionalization of MWCNTs was done by acid (HCl, HNO_3, Aquaregia)and non-acid (NH_4OH/H_2O_2) treatment.All treatments followed with variation of ultra-sonication time.The dispersion of MWCNTs was monitored by UV-VIS absorption spectroscopy. Functionalization removes the impurities present in pristine MWCNTs and adds different functional group on the surface of MWCNTs which helps further dispersion. The chemical change after functionalization of MWCNTwas investigated by FT-IR and Raman spectroscopy. Among four chemical reagents, HNO_3acid treated MWCNTs show higher dispersion than other three. The dispersion increases with increasing the sonication time.*

KEYWORDS:*Functionalization,Dispersion,Multiwalled carbon nanotubes, sonication.*

I. INTRODUCTION

Multi walled carbon nanotubes have much more application in different fields due to its own unique properties i.e. high thermal, electrical,mechanical and chemical properties[1].The solution properties of CNTs have also studied in their surface modification and functionalization.

The MWCNTs has bundles due to strong van der Waals forces between them which reduce their novel properties for further different applications in Nano scale field.And it makes difficult in dispersion of MWCNTs for their utilization.So it is necessary to disperse the carbon nanotubes [2].

The dispersion of CNTs in an aqueous media takes place by two ways. First is chemical method; in this method CNTs was functionalized with different oxidizing agent. After functionalizationpolar groups such as carboxyl groups are introduced on the surface of CNTs, which helps for better dispersionand soluble in any solvent.The treatment of MWCNTs with different oxidizing reagents affects both concentration of oxygen atoms on the surface of MWCNTs and the distribution of oxygen containing functional groups, which affect in dispersion of nanotubes. Second by adsorption of surfactants and decrease the van der Waals interaction and improve dispersion of the MWCNTs[3, 4].In functionalization the role of oxidation is to create functional groups such as carboxyl, hydroxyl etc. group [5].

II. MATERIALSAND METHODS

Chemical Modification of Multi Walled Carbon Nanotubes

Sample 1: MWCNTs (0.1 g)(Iljin Nanotech. Co. Ltd. South Korea)was treated with 6 M of HCl (25 mL) via sonicated for about 15 minutes and the solution was refluxed for about 5 hour. Then the final product was washed with distilled water until pH 7 and filtered by using membrane filter. The final black residue was collected and dried in oven below 100˚c for 1 hour.

Sample 2: MWCNTs (0.1 g)treated with 25 mL, 6M HNO_3. Then the sample was sonicated for 15 minutes and refluxed for 5 hour. After that the MWCNTs was washed with distilled water until pH 7and the filtered by suction filtrate with 0.2µm membrane paper.The final black residue was collected and dried in oven below 100˚C for 1hr.

Sample 3: MWCNTs (0.1 g)was treated with 25 mL, 6M of Aquaregia and sonicated for 15 minutes and reflux for 5 hr. After that the solution of MWCNTs was made neutral by washing with distilled water. Now the solution was filtered

through suction filtrate with 0.2µm membrane paper. Then the final black residue was collected and dried in oven below 100˚C.

Sample 4: of MWCNTs (0.1 g)was treated with 25 mL of NH_4OH/H_2O_2 and sonicated for 15 minutes and reflux for 5 hour. Then it was made neutral by washing with distilled water and filter through suction equipment with 0.2µm membrane paper. At last the black residue was collected and dried in an oven below 100˚C.

Dispersion of F-MWCNTs with Variation of Sonication Time

For the dispersion, 0.0064 g of MWCNTs (sample 1, 2, 3 and 4) was taken separately and 80 mL distilled water was added andkept for ultra-sonication for half hour and kept for 24 hour. After 24 hour the absorbance of sample was recorded from UV-VIS instrument. Similar process was done for 1hour and 2 hour sonication time for all samples. And the dispersion of f-MWCNTs was compared eachother with variation of chemical modification and sonication time.

Measurements

The functionalization was carried out from FTIR (Powder method, SHIMADZO IR100), Raman spectroscopy (Powder method, Horiba Scientific Ltd, with laser excitation 532 nm) and UV-VIS spectroscopy (Solution method).

III. RESULTS AND DISCUSSION

Infrared Spectral Study

FTIR spectrum shows the presence of carboxyl group after chemical treatment that indicates the functionalization of MWCNTs.The figure 1 shows the infrared spectra of pristine MWCNTs, Sample S1, S2, S3 and S4.

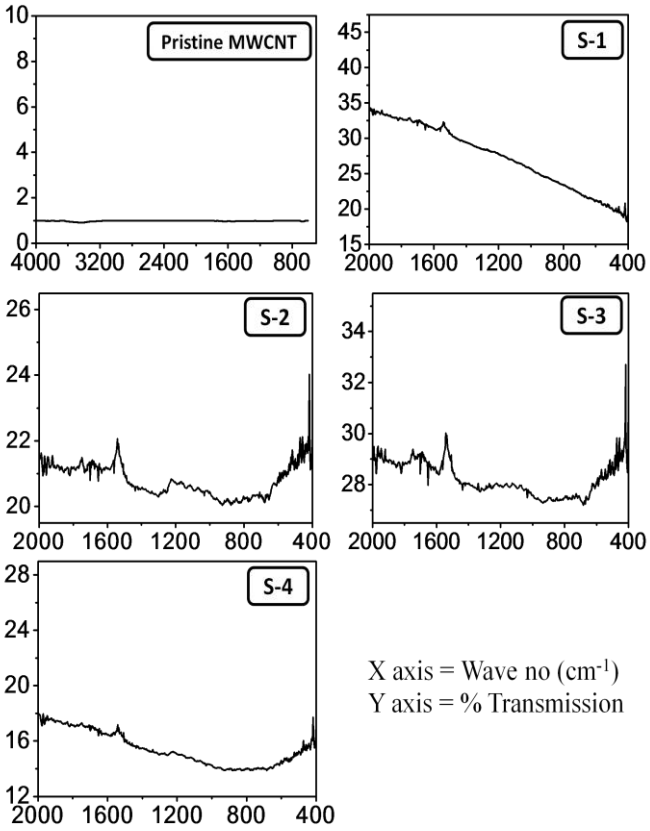

Fig.1. Infrared Spectra of Pristine and Functionalized (S-1: HCl, S-2:HNO_3, S-3:Aqua reiga, S-4: NH_4OH/H_2O_2 treated) MWCNTs.

The IR spectrum of pristine MWCNTs does not show any peaks, it means it does not contain any functional groups. During oxidation process impurities(metal particles and amorphous carbon) are removed fromthe pristine CNTs, but on the other hand several defect sitesare generated on the surface of the CNTs. These defect sitesplay an important role in the functionalization of MWCNTs by different oxygen functional group (Figure 2). The presence of oxygen-containing groups after oxidation process facilitates the exfoliation of CNT bundles, and increases the solubility in polar media.

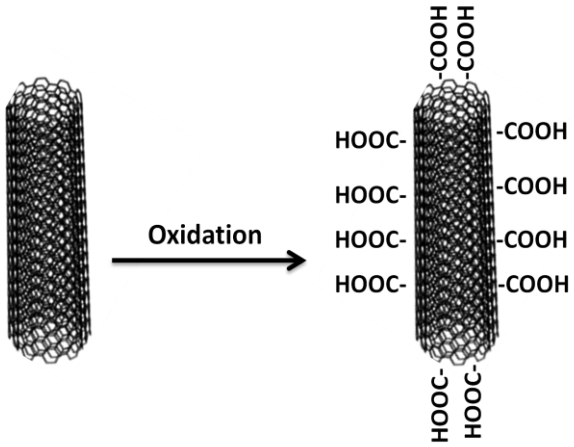

Fig.2. Oxidation of MWCNTs

The IR spectrum of HCl treated MWCNTs doesn't not contain well defined sharp peak because HCl is a non-oxidative acid and cannot introduce oxygen containing groups, but it can enhance the exposure of amorphous carbon encapsulated in graphitic carbon [7]. Many Changes can be seen in the IR spectra of nitric acid, Aqua regia and NH_4OH/H_2O_2treated MWCNTs. Many new peaks are appeared in comparison to pristine MWCNTs.Integrity of hexagonal structure on MWCNTs was confirmed in appearance of peak around 1600 cm^{-1} shows the existence of carbon double bonding (C=C). The peak around 1730-1740 cm^{-1} is due C=O vibration of carboxyl group indicating the presence of carboxylic group [8] on the surface of functionalized MWCNTs. The intensities of these peaks are high in case of nitric acid and aqua regia treated MWCNTs than NH_4OH/H_2O_2treated indicating more oxygen functional groups are added in case of nitric acid and aqua regia treated MWCNTs that NH_4OH/H_2O_2treated. If more oxygen functional groups werepresence there better dispersion should be there. This is shown by UV-VIS absorption study.

UV-Visible Spectroscopy

The dispersion study was done by UV-VIS absorption study. The MWCNTs show absorbance in the UV range from 200-400 nm due to π-π^*electronic transition of aromatic C-C bond in MWCNTs.This electronic transition occurs only by single CNTs not by bundle CNTs. The higher value ofabsorbance indicates the higher dispersion [9].The figure 3 shows the UV spectra of f-MWCNTs with ½ , 1 and 2 hr sonication time.

Figure below showed the UV absorption spectra of chemically modified MWCNTs. Among the four types of chemically modified MWCNTs, the HNO_3 treated MWCNTs has high absorption value. This high absorption indicates the better dispersion of MWCNTs. This may be due to addition of more oxygen functional group on the surface of MWCNTs during oxidation process, which helps the exfoliation of CNT bundles, and increases the solubility in polar media and improve their hydrophilicity. The least absorption occurred in HCl treated MWCNTs. HCl is non- oxidative reagent. No oxygen functional group can be added by this reagent.

From above UV spectra, the dispersion of f-MWCNTs was goes on increasing with increasing in sonication time. During sonication the bundle MWCNTs get de bundalized. The nitric acid MWCNTs give better dispersion among four chemical treated MWCNTs [9].

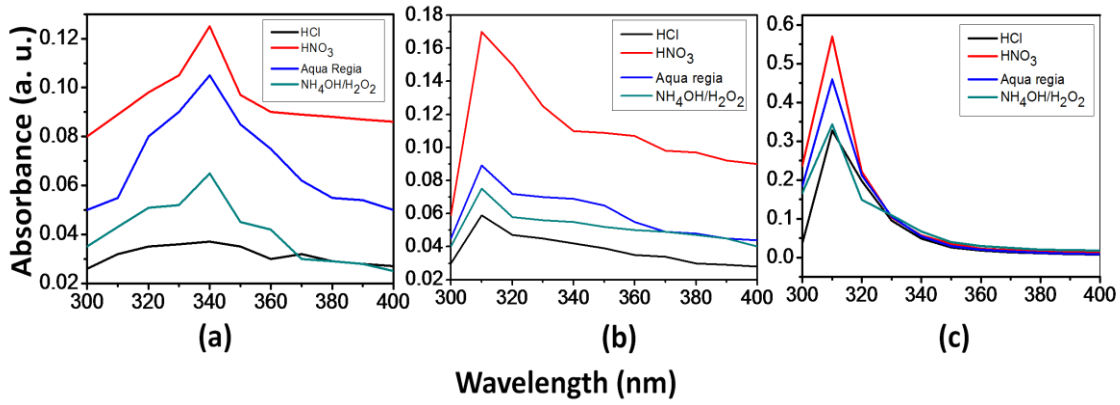

Fig.3. UV Absorption Spectra of Functionalized MWCNTs.(a) 1/2 hour (b) 1 hour and (c) 2 hour sonication time.

Raman Spectroscopy

Raman spectroscopy is a very useful tool forcharacterization of carbon nanotubes andcarbon-based nanostructures. Raman spectra of carbon nanotubes exhibit two characteristics bands around 1340-1330cm^{-1} (D-band) and 1580-1590 cm^{-1} (G-band).The G-band is indicative of well-ordered structure associated with sp^2 carbon atoms in graphene sidewalls. And the D- band can cause by either disorder in the MWCNTs sidewalls, and due to amorphous carbon [10].The structural disorder in carbon is due to the finite or Nano sized graphiticplanes and other forms of carbon, such as rings alongwith defects on the nanotube walls, vacancies, heptagon-pentagonpairs, kinks and heteroatoms.

Figure 4showed the Raman spectra of pristine and chemical treated MWCNTs. The band at 1330 cm^{-1} (pristine), 1340 cm^{-1} (HCl), 1340 cm^{-1} (HNO_3), 1341 cm^{-1} (Aquaregia) and 1341 cm^{-1} (NH_4OH/H_2O_2) indicate D-band. The D-band attributed to the presence of amorphous or disordered carbon in the CNT samples [11]. The band at 1580 cm^{-1} (pristine),1584 cm^{-1} (HCl), 1582 cm^{-1} (HNO_3), 1580 cm^{-1} (Aqua regia) and 1582 cm^{-1} (NH_4OH/H_2O_2) shows G-band, arise from in plane tangential stretching of the carbon-carbon bonds in graphite.

Table5.3: D-band and G-band (cm^{-1}) of P-MWCNTs and HCl, HNO_3, Aqua regia and NH_4OH/H_2O_2 treated MWCNTs.

Band	Pristine	HCl	HNO_3	Aquaregia	NH_4OH/H_2O_2
D-band	1330	1340	1340	1341	1341
G-band	1580	1584	1582	1580	1580
I_G/I_D	0.84	1.14	1.06	1.00	1.25

The intensity ration of G-band and D-band was used to quantify the oxidation process. The I_G/I_D ratio was shown in table 1.First, let's start with the non-oxidative treatment i. e. with HCl. Reduction in intensity of D band has occurred. Increase in the value of I_G/I_D was observed so it can be concluded that treatment with HCl leads to an appreciable elimination of graphitic nanoparticles.

The most pronounced modifications of the Raman modes of MWCNTs were detected for the sample treated with HNO_3 and Aqua regia. This was due to presence of oxygen in their molecular structures and their stronger interaction with the MWCNTs.The I_G/I_D ratio increase in case of nitric acid and Aqua regia treatment indicating oxidative functionalization which supports the destruction of the graphitic integrity and subsequent formation of small graphitic fragments [12].The oxidation process causes a continuous increase in the number of defective sites, which increases the reactivity of the MWCNTs. The distributionof defect sites on the nanotube lattice is due to breaking ofsome of the walls of the MWCNTs by oxidation.These defects include the conversion of sp^2-hybridizedcarbon to sp^3-hybridized carbon during the oxidationprocess, with the creation of oxygen functional group.While in the case of NH_4OH/H_2O_2 treated MWCNTs an enhancement of the I_G/I_Dratio means there is no additional side wall effects on the MWCNTs [1].

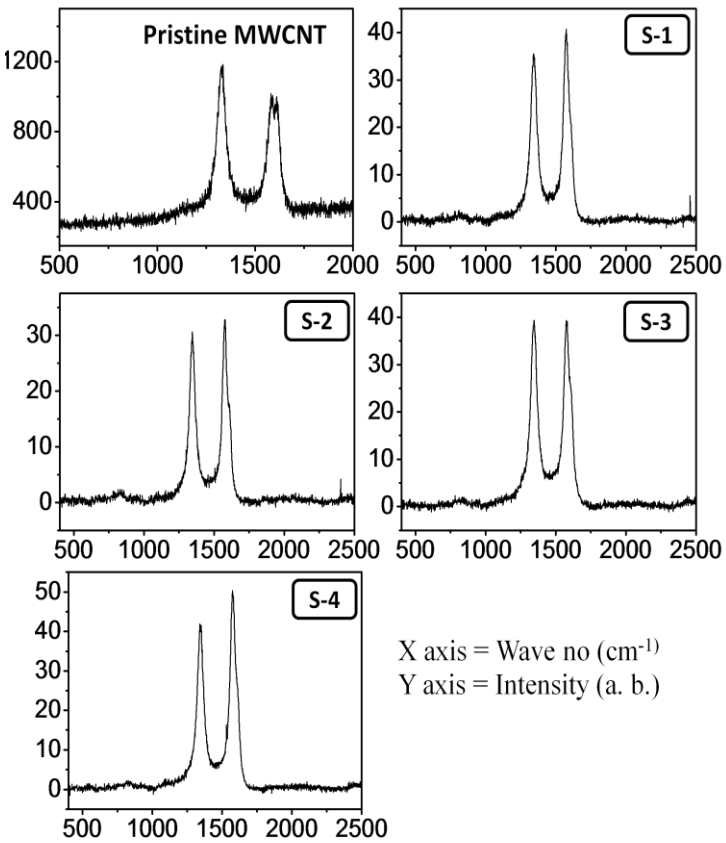

Fig.4.Raman Spectra of Pristine and Functionalized MWCNTs.

IV. CONCLUSION

Chemically modified multiwalled carbon nanotube,

played an important role in dispersion of nanotubes. Differentchemical modification was done in MWCNTs in order to study the dispersion of MWCNTs. The chemical modification of MWCNTs was done by oxidative (Conc. HNO_3, Aqua regia, NH_4OH/H_2O_2) as well as non-oxidative (Conc. HCl) treatment. After, chemical modification with oxidative treatment, different oxygen functional groups was formed on MWCNTs shown by FT-IR spectral studies.

Raman spectroscopy shows the destruction of carbon based nanostructure. Oxidation with HNO_3 and Aqua regia increase the more defect sides rather than other treatments.

This dispersion of MWCNTs was studied by using UV-VIS spectrophotometer. The nitric acid treated MWCNTs show higher absorbance means greater dispersion of MWCNTs among four chemical reagents.Absorbance in UV range is due to transition of π-π^* electron of aromatic C-C bond in MWCNTs. Only dispersed CNTs show this type of transition. The bundle didn't show thistransition. High absorbance means transition of many π-$\pi^*$of individual CNTs take place, indicating good dispersion. The dispersion of MWCNTs goes on increasing with increasing sonication time.

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