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SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES DECORATED MWCNTS

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Abstract-In this paper, silver nanoparticles have been decorated on MWCNTs. Raman and SEM analysis of the final product were done and it was seen that in SEM images there is a little attachment of silver on the nanotubes. As far as Raman spectroscopy of the sample is concerned, the results were quite good. It has been shown by the Raman analysis that by the formation of silver nanoparticles, carbon structure of MWCNTs was modified. Further Gaussian fitting (de-convolution) was done in origin 8.5 and the intensity of the bands in Ag-CNT and pristine CNT were found and there I_D/I_G ratio were calculated. It has been found that upon the adsorption of Ag-NPs, the I_D/I_G values comes to be approximately 1.3 and 1.65 for functionalized MWCNTs and silver decorated MWCNTs samples respectively. The linkage of prepared silver nanoparticles with functional groups on MWCNTs was confirmed from Raman measurements.
Keywords: carbon nanotubes, MWCNT, Tollens process, Raman spectroscopy, SEM.

1. INTRODUCTION

Carbon nanotubes have unique tubular structure that attracts researchers. From the point of view for basic scientific research, CNTs are very useful materials [1]. CNTs have significant applications in various fields like chemical biology, biomedical sciences, air and water filtration devices, electronic devices etc [2]. To enhance the features of CNTs, a lot of research work has been done for modification of CNTs by decorating some nanoparticles on them. Various materials like polymers, biomolecules and organic molecules have been decorated onto CNTs to obtain enhanced featured derivatives [3]. By the deposition of metallic nanoparticles onto CNTs, important hybrid structures has been obtained having enhanced properties valuable for various applications like catalysis, air and water filtration etc. In recent times, decoration of CNTs has been utilized to get better performance in their application areas [4-5]. CNTs decorated with metallic nanoparticles have been utilized in photovoltaic appliance [6]. Also on decoration of metallic nanoparticles on carbon nanotubes, they show magnetic behaviour [7]. Thus integration of metal nanoparticles with CNTs had improved their performance in wide range of applications.

In our present work we have decorated silver nanoparticles on MWCNTs. Raman and SEM analysis of the final product were done and it was seen that in SEM images there is a little attachment of silver on the nanotubes. It has been shown by the Raman analysis that by the formation of silver nanoparticles, carbon structure of MWCNTs was modified. Further Gaussian fitting (de-convolution) was done in origin 8.5 and the intensity of the bands in Ag-CNT and pristine CNT were found and there I_D/I_G ratio were calculated. It has been found that upon the adsorption of Ag-NPs, the I_D/I_G values comes to be approximately 1.3 and 1.65 for functionalized MWCNTs and silver decorated MWCNTs samples respectively. The linkage of prepared silver nanoparticles with functional groups on MWCNTs was confirmed from Raman measurements.

2. DECORATION OF SILVER NANOPARTICLES ON MWCNT

In order to decorate silver nanoparticles on multi-walled carbon nanotubes (MWCNT) we have to follow the steps given below:

- Synthesis of Silver Nanoparticles by Tollens Process
- Acid Treatment of MWCNTs
- Decoration of Ag-NPs on Functionalized MWCNTs

2.1 Chemicals Used:

In the decoration process along with MWCNTs and distilled water, following chemicals have been used: Sulphuric acid (H_2SO_4), Nitric acid (HNO_3), Oleic acid ($C_{18}H_{34}O_2$), Sodium Hydroxide (NaOH), Silver Nitrate ($AgNO_3$), Ammonia (NH_3), glucose ($C_6H_{12}O_6$).

2.2 Synthesis of Silver Nanoparticles by Tollens Process:

The silver nanoparticles were prepared by using a modified Tollens process [8]. First of all, 3.4g of $AgNO_3$ was dissolved in 200mL distilled water by stirring as shown in fig 2.1. Then the resultant solution was precipitated with 0.1511 g of NaOH. This precipitate composed of Ag_2O. The precipitate was filtered and dissolved in 200 ml of aqueous NH_3 to form silver

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ammonium complex $[Ag\ (NH_3)_2]^+$ solution. Then 5 ml of oleic acid was added into the complex drop-wise. The resultant solution was then stirred for 2 hours at room temperature to form a homogeneous reaction mixture. The homogeneous reaction mixture was then reduced by adding 2g of glucose with UV irradiation. For reduction process a UV lamp was used as shown in fig.2.2.

Fig 2.1 disolving $Agno_3$ in water by stirring

Fig 2.2 reduction process by UV lamp

2.3 Acid Treatment of MWCNTs

First of all, to remove carbon from the samples, 100mg of pristine MWCNTs was oxidized for 2 hours at 154ºC using hot air oven as shown in fig. 2.3

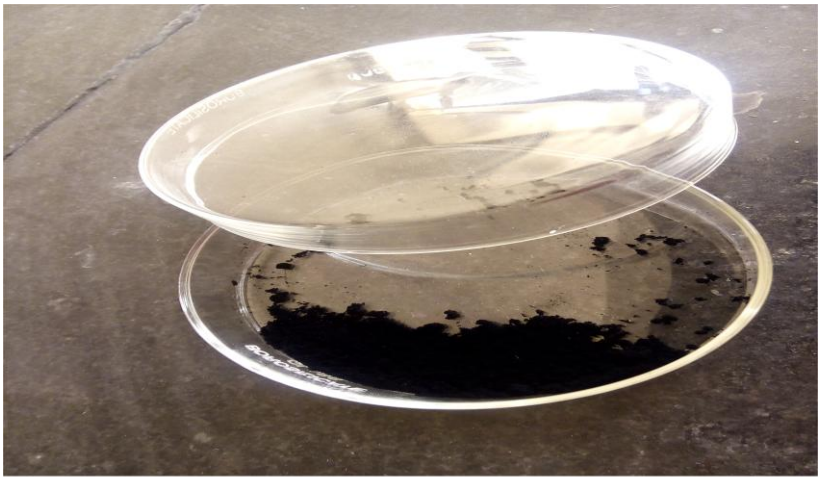

Fig 2.3 Thermally oxidized CNT

Next, 50mg of the oxidized MWCNTs was treated in 120mL of an acid mixture of HNO_3 (30ml) and H_2SO_4 (90ml) (1 : 3 volume/volume) at 65ºC at 900 rpm for 12 h to produce OH^- and/or COOH functionalized MWCNTs. Then the samples were filtered and washed with distilled water. Filtered samples were then allowed to dry under vacuum at 120ºC for 10 h. Finally, 30 mg of the OH^- and/or COOH functionalized MWCNTs was dispersed in 100mL of distilled water for later analysis.

2.4 Decoration of silver nanoparticles on functionalized MWCNTs

Now the decoration of the silver nanoparticles on the OH^- and/or COOH functionalized MWCNTs was conducted. We used the same process for synthesis of Ag-NPs using Tollens process as mentioned in Section 2.2. After the formation of silver ammonium complex, 30mL of functionalized MWCNTs was added with the Ag $[(NH_3)_2]^+$ silver ammonia complex and stirred for 30 minutes. The reduction of the homogeneous mixture was done by the addition of reducing agent glucose (4 g) and stabilizing agent oleic acid (5 ml) in it with UV irradiation. Without extra heating the mixture was irradiated with UV for 10-12 hours along with stirring. After 12 hours UV irradiation, silver nanoparticles were decorated onto functionalized MWCNTs. The resulting solid products of Ag-MWCNTs nanocomposits were collected by centrifugation as shown in fig 2.4

and were purified by distilled water wash and then vacuum dried at 120ºC for 8–10 h. Decorated silver nanoparticles on MWCNTs were shown in fig. 2.5.

Fig 2.4 Final product obtained by centrifugation

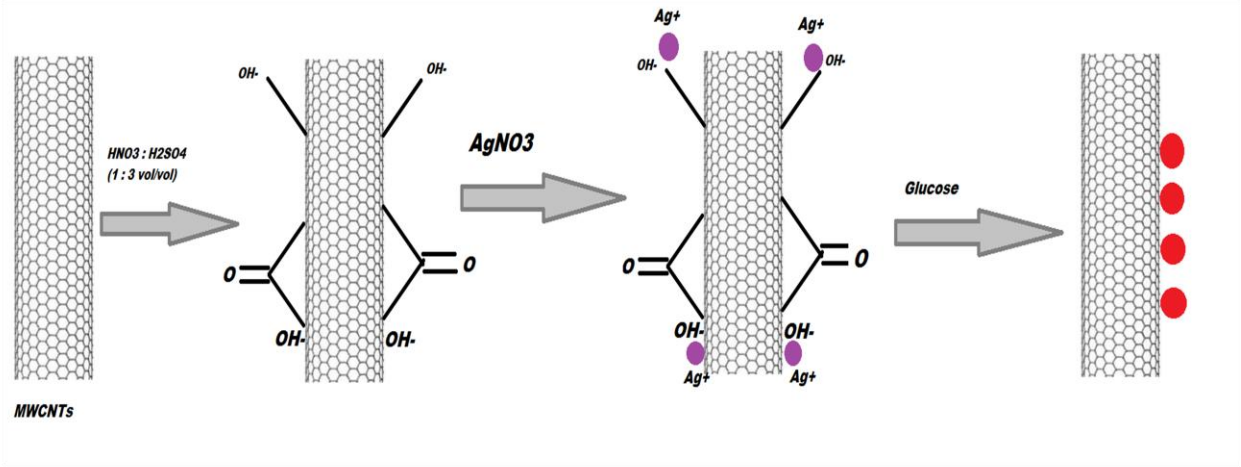

Fig 2.5 Decoration of silver nanoparticles on the multiwalled carbon nanotubes.

2.5 Raman Spectroscopy

2.5.1 Introduction

Raman spectroscopy is a spectroscopy depending on inelastic scattering of monochromatic laser light [9]. It arises due to scattering of photons by the sample, when a monochromatic light is incident on a sample. Scattered photons have frequencies greater than or less than the incident frequency. This phenomenon of frequency shift of monochromatic light after interaction with a sample in called Raman Effect. Here the sample can be solid, liquid or gas [10].

2.5.2 Origin of Raman

Raman Effect arises due to change in molecular polarizability of the sample on interaction with monochromatic radiation. When a molecule having no Raman active mode excites to higher vibrational state then on de-excitation, it will return to the same basic vibrational state emitting photons of same frequency ν_0 as the incident light. This scattering is called as Rayleigh scattering which is elastic. When a molecule having Raman active mode absorbs a photon and get excited to higher Vibrational state, on de-excitation some part of energy, $h\nu_m$ get transferred to that active mode and the scattering photon have a down shift in frequency. This is the Raman Stokes scattering. When a molecule with Raman active mode already in higher Vibrational state absorbs a photon, on de-excitation it gets up shift in frequency [11]. This is called the Anti-Stokes Raman scattering as shown in fig.2.6.

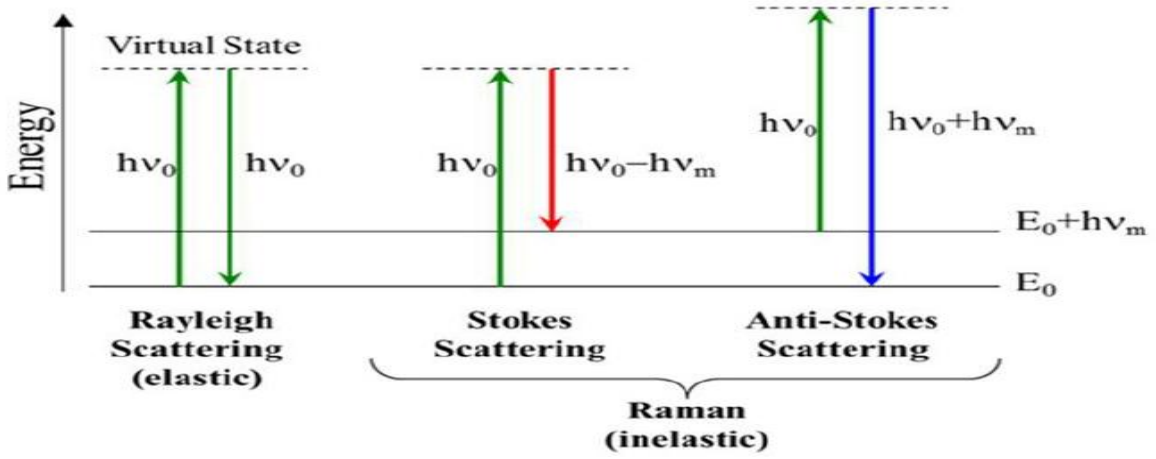

Fig.2.6: Raman transitional Schemes

In Raman spectroscopy, 99.999% of incident photons undergo elastic Rayleigh scattering which is useless for molecular characterization purposes. Only 0.001% of the incident radiations undergo inelastic Raman scattering which is utilized in practical purposes like molecular characterization [12]. This inelastic Raman signal is very weak therefore special instruments like tuneable filters, laser stop apertures are used to obtain batter quality Raman spectra [13].

2.5.3 Raman Spectroscopy Of Cnt's

Different studies on MWCNT doped by acids were reported previously. In particular, doping by a mixture of HNO_3 and H_2SO_4 are very interesting, also Raman analysis of UV treated functionalized CNT was done. The vibronic properties of carbon nanotubes can be modified by the introduction of guest molecules to their structure. By using Raman spectroscopy, diameter distribution, chirality, structure and purity of CNTs can be determined [14].

Raman Spectra provides much more information about CNTs. The most important features of CNTs informed by Raman are radial breathing modes, D-band and G-band shown in fig.2.7. D band is called as defect mode which is a longitudinal optical phonon. This is located between 1330 and 1360 cm^{-1}. It exits in all carbon allotropes. G band is called as graphite mode which is tangential shear mode of carbon atoms corresponding to stretching mode of graphite plane. This is located between 1580 and 1630 cm^{-1} [15].

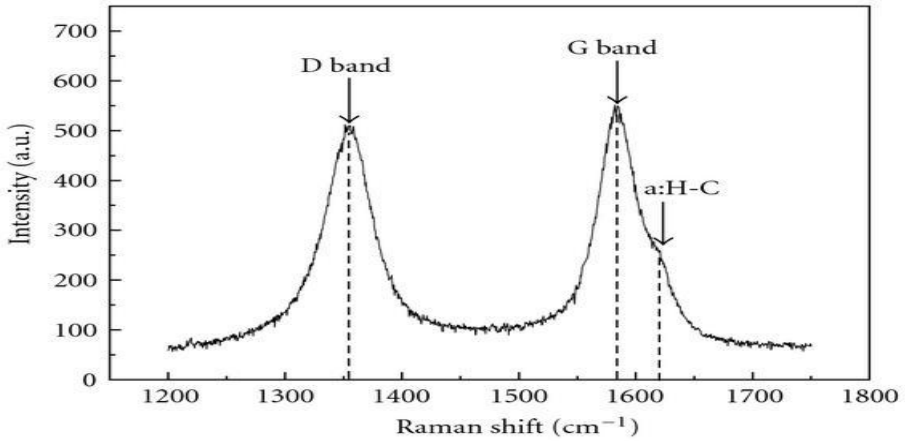

Fig.2.7: D band and G band of CNTs

2.6 Scanning Electron Microscope (Sem)

SEM is used for production of high resolution image of a sample. In this microscope a finely focused beam of electrons is used. It provides a three dimensional image of the sample which is very useful for examination of surface structure of a sample [16].

2.7. Working Principle Of Sem

SEM uses an electron gun for examination of a specimen. The electron gun is located at top of the instrument and it shoots out highly concentrated electrons beam [17].

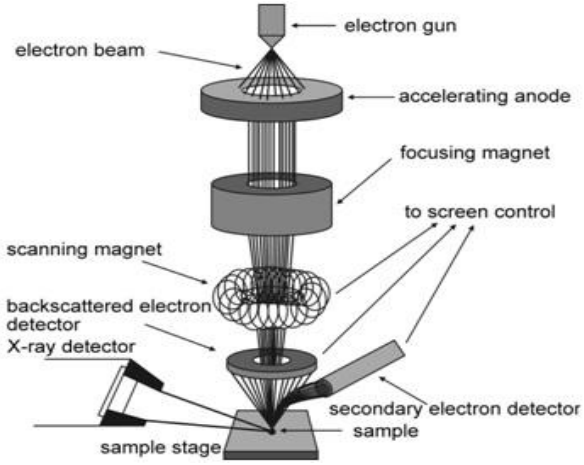

Fig.2.8: Scanning Electron Microscope

It consists of a series of lenses inside a vacuum chamber. These lenses are used for concentrating the electrons beam to the specimen. Magnification of the SEM is directly proportional to the concentration of electrons. For perfect image of specimen, vacuum chamber is required so that highly intense beam would not be deflected by the small particles in the surroundings of SEM. When a highly intense beam is incident on a specimen, it emits three types of electrons along with X-rays. Primary and secondary backscattered electrons are picked up by an electron recorder and imprint was recorded. This recorded imprint is transformed into a clear image which provides information about the surface morphology of the specimen [18-19].
One of the best advantages of scanning electron microscope is that it provides textual information in a consistent way. Traditional scanning electron microscopes were not able to provide colour images. However, now a days, more advanced technologies have allowed researchers to capture a clear and consistent image of the sample's reaction to the incident intense electron beam. Thus SEM provides significant information about size and topography of the sample clearly [20-21].

3. RESULTS AND DISCUSSION

3.1. Formation of Ag-NPs on functionalized MWCNTs

For synthesis of Ag-MWCNTs nanocomposits, a step by step process is shown in fig. 2.5. The Tollens process enables us to produce silver colloids with small sizes and stable aqueous dispersions at high yield. In our present work, we employed this process to decorate silver NPs on the surface of pristine MWCNTs. Raman spectra of pristine MWCNTs is shown in fig.3.1.

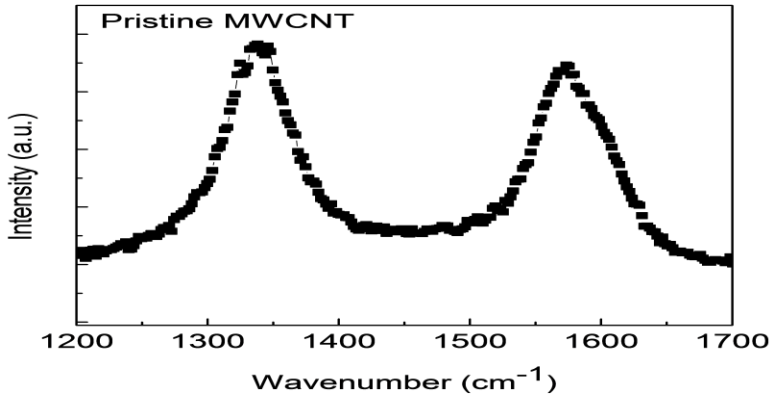

Fig 3.1 Raman spectra of pristine MWCNT

In a two-step process, the first step of the acid treatment of MWCNTs is to create functional groups having oxygen on the exterior of MWCNTs whose Raman spectra is shown in fig.3.2. These functionalized groups make the MWCNTs well dispersed in aqueous medium with high stability. The purpose of surface modification of MWCNTs is to introduce more binding sites for anchoring the precursors of silver ions or silver NPs. In second step, the silver NPs were formed on the functional groups of MWCNTs via reduction of silver ions by glucose with assistance of UV irradiation in Tollens reaction. The formation of silver nanoparticles on the exterior of MWCNTS was confirmed using SEM images.

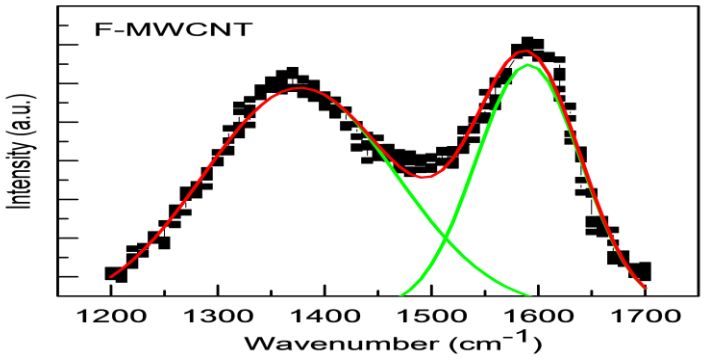

Fig 3.2 Raman spectra of Functionalized MWCNT

3.2. Interaction of silver nanoparticles on the exterior of MWCNTs

To elucidate the interaction of Ag-NPs with functional groups on the surface of MWCNTs, Raman analyses were conducted. Raman spectroscopy was used to investigate the crystallinity and the structural changes of carbon framework of MWCNTs. As one can see from Figure 3.4, the Functionalised MWCNTs shows major peaks at 1350cm^{-1} and at 1580 cm^{-1}, and equivalent peaks for Ag decorated MWCNTs found at 1360 cm^{-1} and 1590 cm^{-1}.

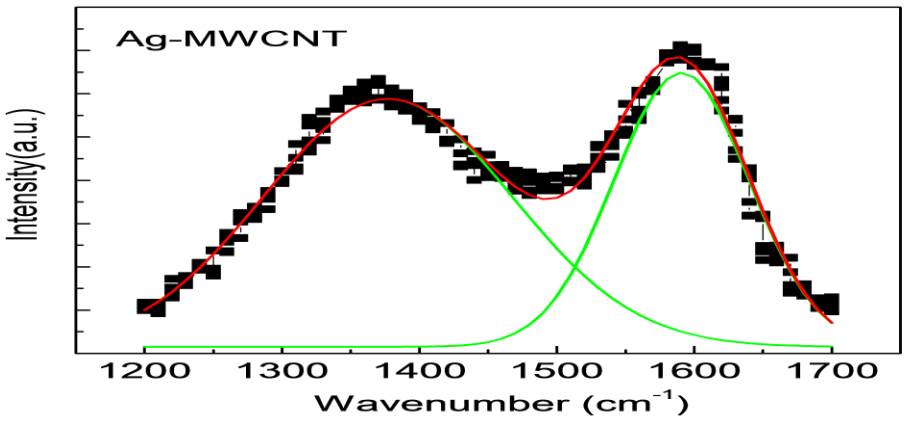

Fig 3.3 Raman spectra of Ag-MWCNT

In silver decorated MWCNTs, a considerable shift in frequency towards small wave-number of d made is observed as compare to functionalized MWCNTs. This results in increased disorder of grapheme layers and increment of defects due to partial reduction of MWCNTs by glucose. Raman analysis showed the modification in carbon structure of MWCNTs due to decoration of Ag-nanoparticles on MWCNTs.

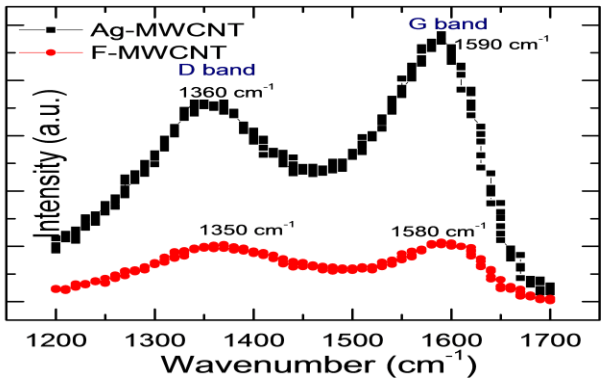

Fig 3.4 Comparison of F-MWCNT and Ag-MWCNT Raman spectra

Also the intensity ratio of the D band and G band is also increased on decoration of Ag-nanoparticles on MWCNTs. This intensity ratio represents the extent of disorder and sp^2 Domain size. The previous studies revealed that the MWCNTs without surface modification would lead to poor dispersion and formed large particles sizes because of deficiency of proper binding sites for anchoring silver nanoparticles. Therefore, surface functionalization of CNTs is necessarily important step to enhance the surface binding sites, avoid the aggregation of silver nanoparticles, improve dispersions, and reduce the particles sizes of nanoparticles. Indeed, the functional groups on exterior of MWCNTs would produce the nucleation sites for deposition and dispersions of silver nanoparticles on the exterior of MWCNTs. The linkage of prepared silver nanoparticles with functional groups on the surface of MWCNTs was confirmed from Raman measurements.

The use of Tollens process with UV irradiation enables us to produce small particles size of silver nanoparticles and high aqueous dispersions. The UV irradiation plays a main role in achieving high dispersions of silver nanoparticles on the surface of MWCNTs and their size distribution. The pristine and Ag-MWCNT surfaces can be seen in SEM images, which show the attachment of silver on CNT in fig.3.5 and fig. 3.6 respectively.

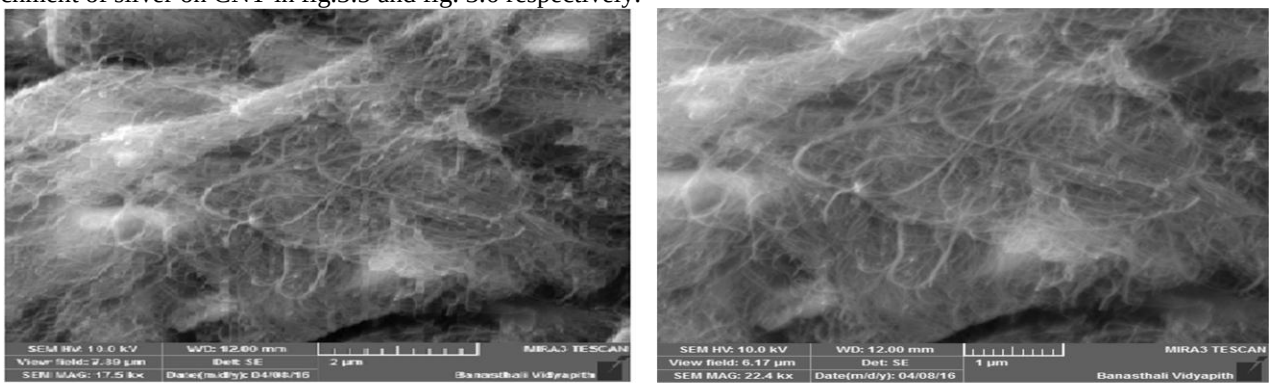

Fig 3.5 Sem images of pristine CNT

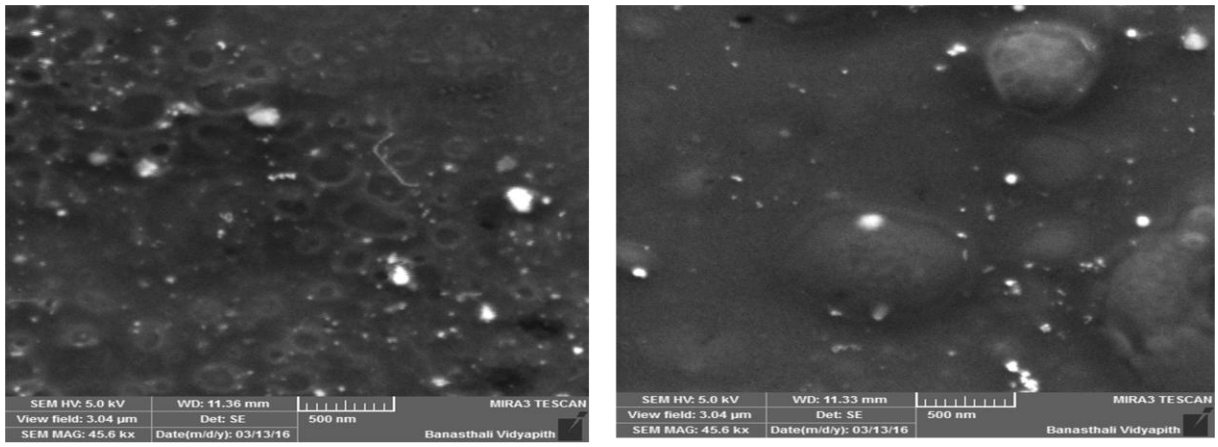

Fig 3.6 SEM images of Ag-CNT

4. CONCLUSIONS

In our present work we have decorated silver nanoparticles on MWCNTs. Raman and SEM analysis of the final product were done and it was seen that in SEM images there is a little attachment of silver on the nanotubes, the clarity of SEM images was somewhat less than pristine CNT, which may be due to intensity differences while doing SEM.

As far as Raman spectroscopy of the sample is concerned, the results were quite good. In silver decorated MWCNTs, a considerable shift in frequency towards small wave-number of d made is observed as compare to functionalized MWCNTs. This results in increased disorder of grapheme layers and increment of defects due to partial reduction of MWCNTs by glucose during the synthesis process. The Raman analysis revealed the modification in structure of carbon of MWCNTs after decoration of silver nanoparticles. Further Gaussian fitting (de-convolution) was done in origin 8.5 and the intensity of the bands in Ag-CNT and pristine CNT were found and there I_D/I_G ratio were calculated. Also the intensity ratio of the D band and G band is increased on absorption of metal nanoparticles. The I_D/I_G values were approximately 1.3 and 1.65 for F-MWCNTs and Ag-MWCNTs samples, respectively. Linkage of prepared silver nanoparticles with functional groups on the surface of MWCNTs was confirmed from Raman measurements.

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