

Synthesis and characterization of functionalized CNTs using soya and milk protein

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Abstract Nanotechnology is the study of the phenomenon and manipulation of matter at atomic and molecular scale to enhance their older property and generate several new properties. Carbon nanotubes (CNTs) are one of the most commonly mentioned building blocks of nanotechnology. CNTs are very prevalent in today's world of medical research and are being highly researched in the fields of efficient drug delivery and bio sensing methods for disease treatment and health monitoring. There are number of methods for synthesizing CNTs. This is a biological method for synthesis of CNTs in which protein is used as carbon source and amino acids present in protein form complex with metal salt. The CNTs synthesized are then characterized and functionalized using techniques such as transmission electron microscopy, Fourier transform infrared, nuclear magnetic resonance, ultra-violet visible spectroscopy, X-ray diffraction, etc. The properties of the synthesized CNTs are studied with the help of techniques such as thermo-gravimetric analysis, differential thermal analysis, and vibrating sample magnetometer, etc.

Keywords Amino acids · TEM · VSM · FTIR · IR · UV · TGA · DTA · XRD · Chemical structure

Introduction

Carbon nanotubes (CNTs) are allotropes of carbon. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat (Dresslhw et al. 2008). Due to their exceptional properties a new method is developed using amino acid. The CNTs formed are already functionalized and can be used directly in various applications like targeted drug delivery. In targeted drug delivery, CNTs need to be functionalized so that drug should be attached with it (Bianco et al. 2005; Elhissi et al. 2012).

Experimental details

In the preparation of CNTs by chemical method the concentration of carbon at a particular point should be high. Without satisfying this condition CNTs cannot be prepared by this method. So protein is taken as carbon source and cobalt salts are taken as catalyst. The choice of protein is because of the presence of two connecting sites ($-NH_2$ and $-COOH$) within one single molecule. Due to the presence of two connecting sites and Co^{2+} , present in cobalt salt different protein chains are clubbed together and hence concentration of carbon at a point is increased (Tiwari et al. 2011). The major source of protein is Amway protein which is a mixture of soya and milk protein. This protein powder is manufactured by Nutrilite, USA which is a renowned dietary supplement company. As per the claims of the company 100 g of Amway protein contain 85 g of protein and 17 amino acids.

Synthesis of CNTs using Protein and metal salt is a two-step process. In first step a complex of protein and metal

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salt is prepared and dried. In second step the dried material is decomposed in the muffle furnace to obtain CNTs. For the preparation of CNTs using Amway protein (blend of soya and milk protein) in aqueous solution, first 1 N solution of CoCl_2 is prepared in water and 20 ml of it is mixed with 20 g of protein blend for the reaction. The reaction mixture is kept undisturbed for 24 h for self-precipitation of complex. After 24 h jelly like pink complex is formed. The complex is then kept in desiccators for around 7 days. After 7 days the complex is washed with water and dried again. The weight of dry complex is 30.65 g. The complex is now ready to decompose and for further studies.

The complex formed is decomposed at 850 °C in a muffle furnace. For decomposition 25 g of complex is weighed and kept in crucible. The complex is then kept in muffle furnace for 10 min at 850 °C. The weight of decomposed complex is 4.489 g.

Purification of CNTs formed

Purification is also a two-step process.

Step 1: In first step the CNTs are heated in the furnace to remove volatile contents. At the time of decomposition significant weight loss of around 80 % material is observed.

Step 2: In second step the metal content is removed. For removal of metal contents 4.489 g of the CNTs were mixed with HCl. 6 ml of 12 M HCl is taken per grams of CNTs. The mixture is kept as such for 24 h. After 24 h the material was centrifuged and washed with water for several times. The purified CNTs were then filtered and dried. The dry weight of purified CNTs was 3.667 g.

Results and discussion

Characterization is carried out in two steps:

Step I: characterization of amino acid metal complex

The chemical compound prepared by reaction of protein and metal salt is characterized using NMR and IR.

NMR

The NMR spectra of compound prepared by the reaction of Cobalt salt and Amway protein in aqueous medium are shown in Fig. 1 and Table 1.

UV-visible spectroscopy result

The UV spectra of compound prepared by the reaction of Cobalt salt and Amway protein in aqueous solution are shown in Fig. 2 and Table 2.

IR spectroscopy result

The IR spectra of compound prepared by the reaction of Cobalt salt and Amway protein in aqueous solution are shown in Fig. 3.

The IR spectrum describes the presence of different functional groups at various absorption bands which is illustrated in the following Table 3.

On the basis of NMR, UV and IR results the following structure of amino acid is deduced.

Chemical interpretation

The above results show the presence of following groups in the chemical compound. The structure deduced by the following results was containing NH_3^+ , COOH^- , aliphatic amines. The structure deduced was $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_4$. It is very closely related structure to the amino acid-LYSINE.

Formula: $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$

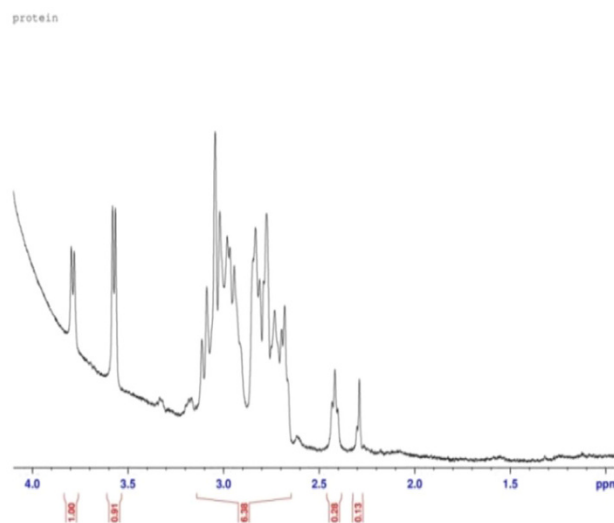
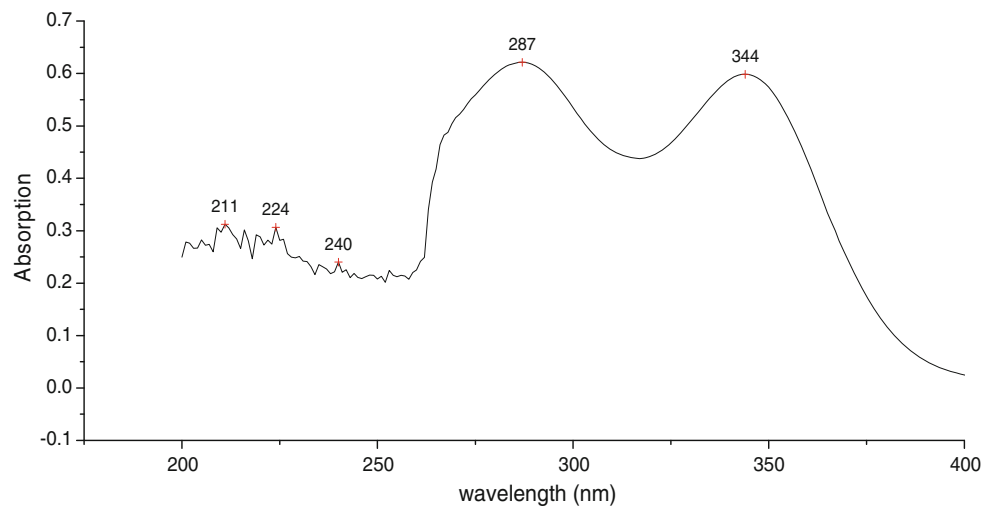


Fig. 1 Graph of NMR illustrating ppm

Table 1 Results of NMR

PEAKS [ppm]		Chemical compound (functional group)	Chemical shift (δ)
Starting point	End point		
2.25	2.31	R-NH ₂	0.13
2.37	2.45	R-CH-OH	0.28
2.65	3.15	R-CH-O	6.38
3.55	3.62	R-CH-NR ₂	0.91
3.75	3.85	R-CH-NR ₂	1.00

Fig. 2 Graph of UV plotted between absorption and wavelength (nm)**Table 2** Results of UV

WAVELENGTH (nm)	Absorption	Compounds
211	0.3	Amides
224	0.3	(CH ₃) ₂ N
287	0.6	ACETONE
344	0.6	NITRO

Composition: C (49.3 %), H (9.65 %), N (19.16 %), and O (21.89 %)

Isotope composition: C (49.3 %), H (9.65 %), N (19.16 %), O (21.89 %)

Mass: 146.1876

Exact mass: 146.105527702

Step II: characterization of CNTs after decomposition and purification

Purification is carried out using TEM and XRD. The fictionalizations are studied using FTIR.

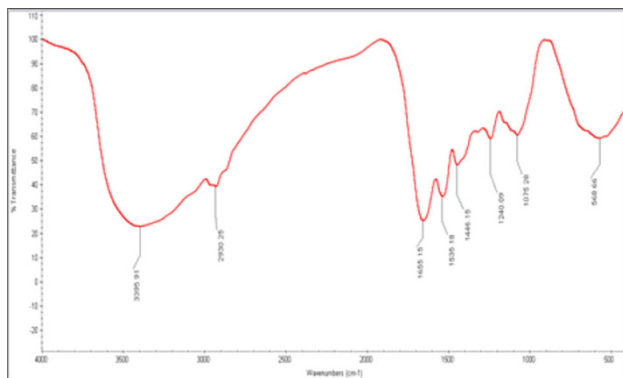
TEM result

TEM images of CNTs are shown in Fig. 4. In TEM images CNTs are clearly visible (Pawlyta et al. 2012). The diffraction pattern of electron bombarded on the sample is given in Fig. 5. It shows the rings of different magnitude which validate the “POLY-CRYSTALLINE” structures of CNTs (Awasthi et al. 2011).

XRD result

XRD graph of CNTs is shown in Fig. 6. The graph shows that the intensity of the peaks is in the range of 25.0–25.9. The results were found to be almost similar to the results reported by for multi-walled CNTs prepared by Bhattacharji et al. (2011) by pyrolysis of turpentine oil ($2\theta = 25.6$) and with Ioan Stalin et al. (2007), who prepared CNTs by catalytic pyrolysis of phenol formaldehyde resin ($2\theta = 26.2$).

This confirms the formation of multi-walled CNTs which proves the existence of CNTs in the sample.

**Fig. 3** Graph of IR plotted between % transmission and wave number**Table 3** Results of IR

Frequency, Cm ⁻¹	Bonds	Functional group
1,075.28	C–N stretch	Aliphatic amines
1,240.09	C–N stretch	Aliphatic amines
1,446.15	C–C Stretch (in ring)	Aromatic
1,535.18	N–O asymmetrical	Nitro compound
1,655.55	–C = C– stretch	Alkene
2,930.25	Carboxylic acid	–COOH
3,395.91	N–H stretch	1°–2° Amines, amides

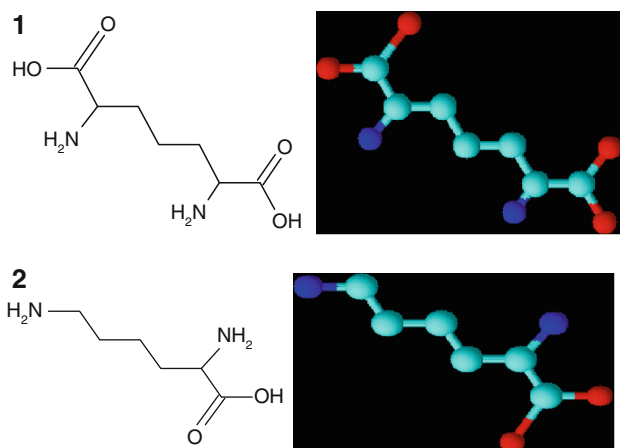


Fig. 4 **1** Deduced chemical structure. **2** Chemical structure of Lysine

FTIR results

The Fourier transform infra-red test of the CNTs synthesized is carried out. The FTIR spectra are illustrated in

Fig. 7. The graph tells about the various functional groups present in the CNTs formed which is described in the Table 4

Study of properties of CNTs Magnetic and thermal properties of CNTs were studied using VSM, TGA-DTA.

Study of magnetic properties Magnetic properties of CNTs are studied using VSM.

VSM results

The magnetic properties of CNTs can be deduced using VSM. The sample of CNTs prepared by us is analyzed using VSM and a graph is plotted between magnetic field and magnetic moment. A blank/reference graph is also prepared taking the same value of magnetic field for ready reference. It is observed that the magnetic moment of the sample is more than the magnetic moment of the blank. This shows the paramagnetic behavior of the CNTs

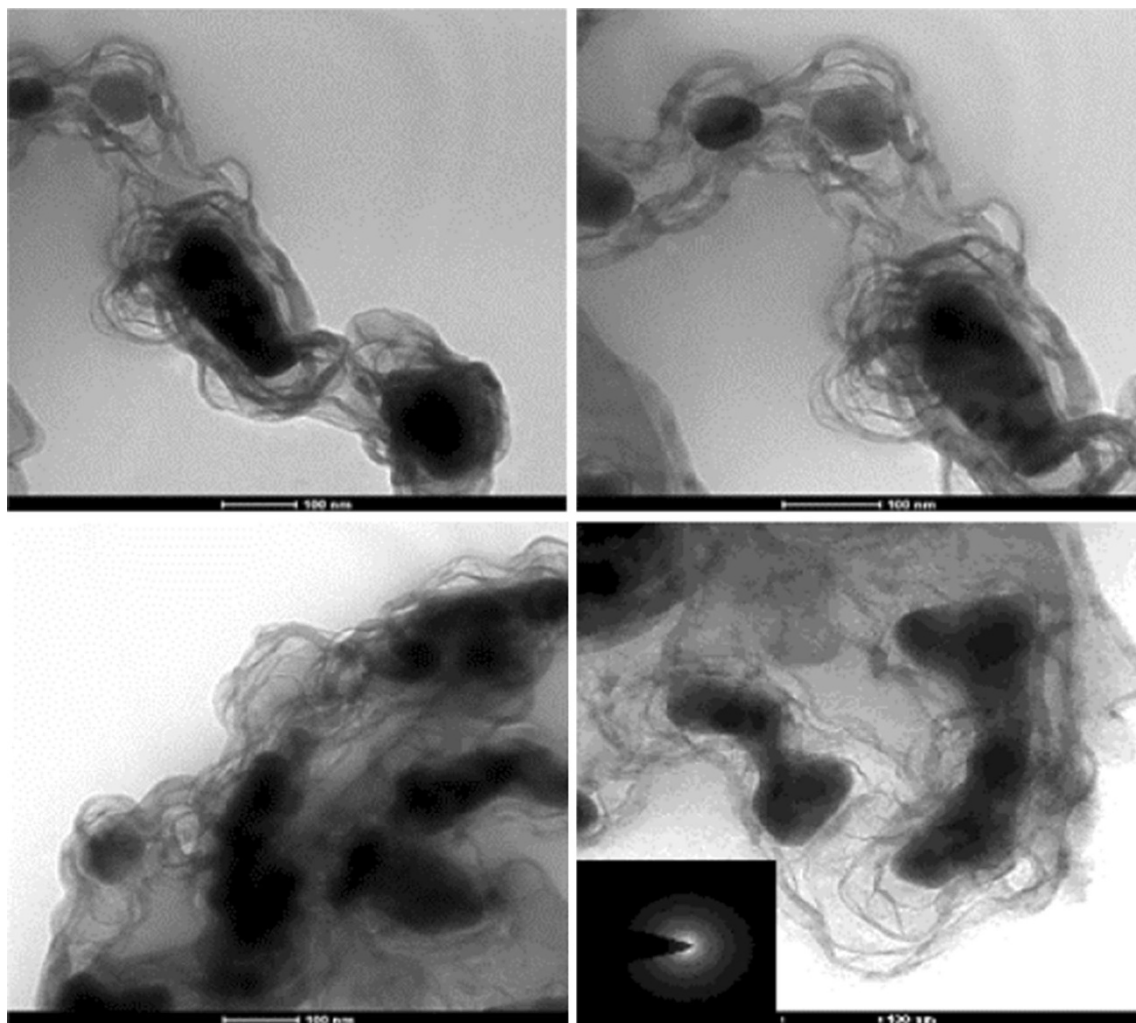


Fig. 5 Results of TEM at magnification of 100 nm and diffraction pattern

Fig. 6 Graph of XRD plotted between lin (counts) and 2theta scale [wider range]. Graph of XRD plotted between lin (counts) and 2theta scale [CNTs range]

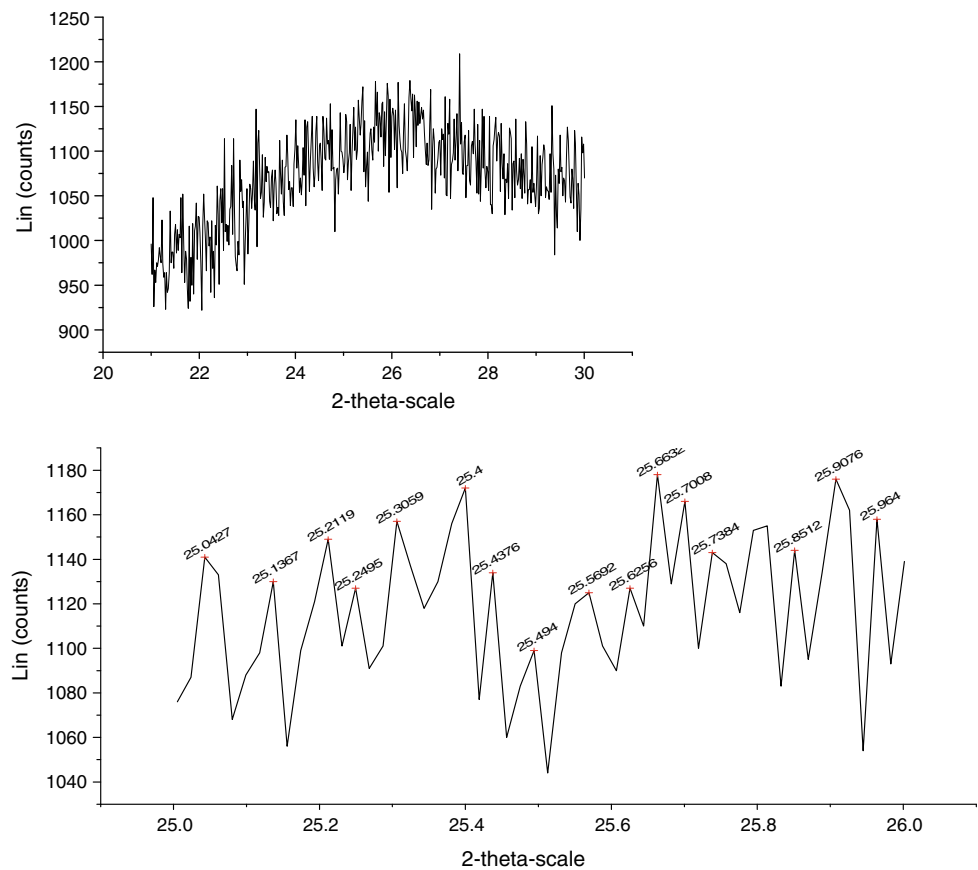
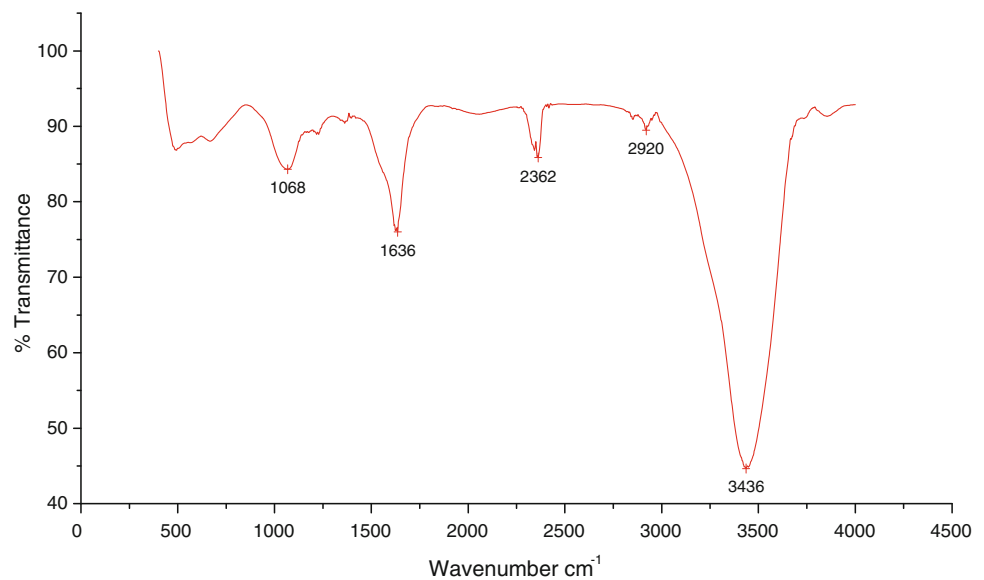


Fig. 7 Graph of FTIR plotted between % transmission and wave number

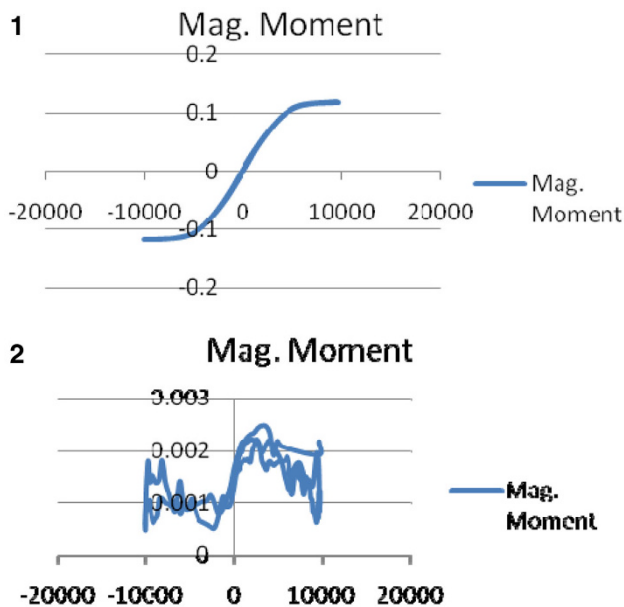


produced (Tiwari et al. 2012). CNTs are usually diamagnetic in nature in our sample all free cobalt ions are removed during process of purification. The magnetic nature can be because of cobalt ions embedded inside the tube. LI Wei-Xue et al. (2007) studied the magnetic properties of multi-walled carbon nanotube encapsulated

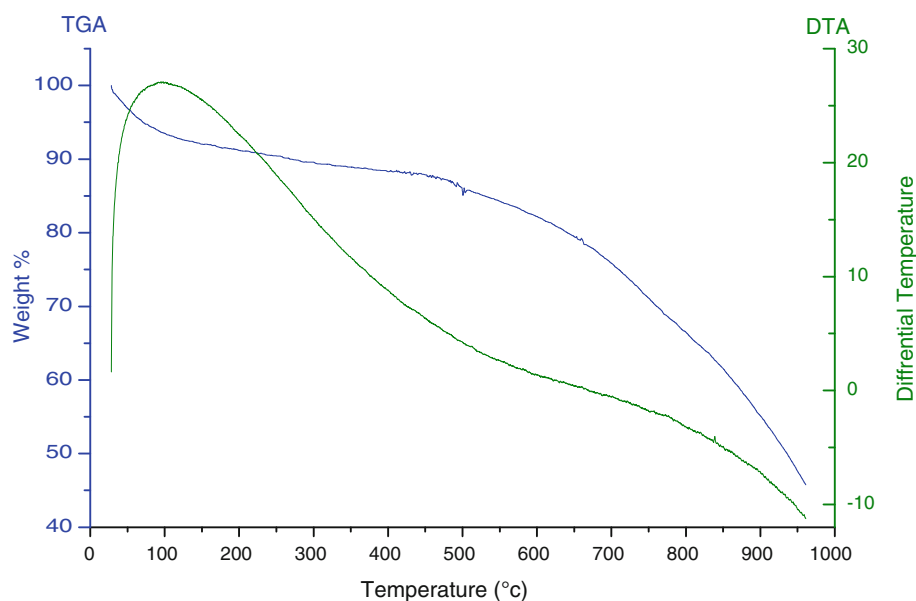
Fe/Co particles. Their graph shows resemblance with the graph of my sample. In both the graphs CNTs are paramagnetic in nature. Graphs show an increase in magnetic moment with increase in magnetic field strength. K. Atre et al. (2008) of Nanomaterial and nano research laboratory, USA synthesized vertically aligned carbon nanotubes.

Table 4 Results of FTIR

Frequency cm^{-1}	Bonds	Functional group
1,068	C–N stretch	Aliphatic amine
1,636	N–H bend	1° amine
2,920	C–H stretch	Carboxylic acid
3,436	O–H stretch	Phenol

**Fig. 8** 1 VSM graph for sample. 2 VSM graph for reference/blank

They also studied magnetic properties using VSM. Their VSM graph also showed similar findings and resembled with the graph of our sample (Fig. 8).

Fig. 9 Graph of TGA-DTA plotted between temperature, weight % and differential temperature

Study of thermal properties The thermal properties of CNTs formed are studied using TGA and DTA.

DTA-TGA result

TGA-DTA analysis of CNTs was carried out in the atmosphere of Nitrogen.

The following graph shows the relation between the temperature and weight% loss and temperature. It also shows high thermal conductivity and thermal stability of CNTs formed. Chang et al. (2004) studied thermal properties of multiwall carbon nanotubes dispersed in water and associated with biological effect using TGA and DTA. Sumio Iijima et al. (2007) also studied the thermal properties of carbon nanotubes ultrasonicated in monochloro benzene (Fig. 9).

The results of all the tests show that the sample contains multi-walled carbon nanotubes that are formed. TEM analysis results show that the nanotubes so formed were of 100 nm size and structurally polycrystalline. FTIR results show that CNTs are functionalized. The properties of the compound formed were also studied using VSM, TGA-DTA. VSM results shows that the CNTs formed are paramagnetic in nature. The paramagnetic nature can be because of nickel ions embedded inside the tube.

TGA-DTA result shows that as with the increase in temperature the % weight of the sample decreases. The results of DTA-TGA show that CNTs have high thermal conductivity and their thermal stability is high.

The methodology used for preparing the CNTs was chemical and biological and shows successful decomposition of protein and metal complex into CNTs.

Conclusion

The sample formed was analyzed using a number of characterization techniques such as TEM, XRD, FTIR, IR, UV, and NMR.

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