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Synthesis of composites by doping of CNTs with nano Fe particles and its ignition through photo flashing

S. SHAH[a,*], H. NASIR[a], A. MATEEN[b], F. AZIZ CHISHTI[a], F. KHATTAK[a], I. YOUSAF[a], S. ULLAH[b],
A. QADEER MALIK[a]
[a]*Chemical Engineering Department, School of Chemical and Materials Engineering, National University of Science and Technology, H12 Islamabad 44000, Pakistan*
[b]*Institute of Space Technology, Islamabad 44000, Pakistan*

Fe-CNTs composite was synthesised by doping of MWCNTs (multi walled carbon Nano tubes) with Nano Fe particles. Initially the received CNTs were purified and activated by functionalization with OH and COOH groups. Then CNTs were doped with various Fe concentrations by simply adjusting weight (wt) ratio of Ferrocene. The composite was ignited by exposing it to an ordinary photo camera flash. It was observed that ignition of the composite was achieved with minimum 16% Fe concentration by wt. The composite was characterized by using FTIR, EDS, FE-SEM, TG/DTA and XRD techniques. Fe-CNTs composite displayed its decomposition around 350 ^{o}C instead of 600 ^{o}C as compared to the oxidation of as received or pristine CNTs. In that study a novel and versatile technique was engineered to synthesise the composite, which may also be used for adsorbing many other metals on the surfaces of CNTs for their application in numerous fields.

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1. Introduction

Recently, extensive studies and investigations on the applicability of CNTs as adsorbent have been undertaken [1, 2]. The excellent adsorption ability through functionalization has ascribed due to increase in their hydro philicity and greater exposure of surface area to the adsorbing species [3]. This exceptional property of CNTs along with the possibility to modify their exterior by doping with foreign materials further enhances their applications. Moreover, being remarkably small in sizes and the extraordinary light absorption characteristics of these Nano tubes lead to their rapid heating under the intensive but brief light flash, which makes it a very attractive species for researchers. This phenomenon is not observed in tightly packed MWCNTs or a solid graphite. Instead, it is only possible when loosely packed SWCNTs absorb the flash energy, which is not easily dissipated. However some researchers propose that the residual content of Nano metal particles assists this ignition [4].

The fabrication of Metal-CNTs composites is of a great interest. Since these composites combine the unique properties of metals or metal oxides and CNTs. In addition to this some extraordinary properties are also exhibited, caused by the interaction between them [5]. So far various techniques have been developed to synthesize CNTs based composites, including the conventional impregnation method [6]. With these techniques, many types of Nano metal particles were decorated on CNTs surfaces and in result low temperature oxidation of CNTs based composites was achieved [6,7]. Among these composites, magnetic CNT composites are of particular interest [8]. The other important aspect of such composites is related to its ignition with an ordinarily camera flash [9]. It has also been demonstrated that the photo ignition effects in CNTs are attributed to their rapid increase in temperature, resulting from absorption of the light flash. The presence of Nano metal particles plays a key role in early ignition of these tubes, higher the content of metal, easier the ignition of CNTs [10]. To synthesize a desired composite, functionalization of CNTs is a primary step. It is essential for improving the solubility and dispersion of nanotubes in aqueous solutions and to design new hybrid materials. Functional groups, attached on the tubes surfaces are found responsible for the various physicochemical and catalytic properties of material [11, 12].

In this work a study is presented with focus remains on three major aspects i.e. Functionalization/Activation of MWCNTs, Synthesis of Fe-CNTS composite and its Ignition under the effect of a photo camera flash. Here an effective technique for the synthesis of the composite is proposed. Through this method Nano Fe particles are decorated on MWCNTs surfaces. Ferrocene is used as Fe precursor and initial mass ratio of Ferrocene is controlled to manipulate the concentration of adsorbing Nano metal particles. However purification and activation of CNTs are carried out prior to the synthesis of Fe-CNTs composite. The engineered technique used for doping of CNTs with Nano Fe particles is a versatile process, through which various metals e.g. Zn, Mg, and Al etc. may also be decorated on CNTs and many types of composite can be fabricated. Ignition of Fe-CNTs composite by photo flashing makes it suitable for application as a smart micro initiating device and a source of high energy.

2. Experimental Method

MWCNTs, purchased from Sigma Aldrich were of purity: > 95%, SSA: > 500 m^2/g, outside diameter: < 25 nm, length: 10-30 um, called as pristine CNTs. These were sonicated in 70% concentrated nitric acid in order to open their agglomeration and anchoring acid solution uniformly on the tubes surfaces. The same sonicated mixture was oxidized through wet oxidation by refluxing CNTs-HNO_3 solution for 4 hours. That process was followed by centrifuge and washing of activated CNTs. A black sediment was found at the bottom of the tube and brownish supernatant was decanted off. The sediment was repeatedly re suspended in double distilled water by vigorously shaking and followed by centrifugation and decanting the supernatant. Such washing was done 5 times until the pH value was found neutral. The final product was heated in air at 110 °C for 12 hours in order to remove moisture and dry the CNTs paste. Same solid CNTs were again heated at 350 °C for 2 hours to remove the amorphous carbon, resultantly fluffy powdered CNTs were obtained. At the end of this treatment activated CNTs with OH and COOH functional groups were produced.

The activated CNTs were taken as a starting material and Ferrocene in different wt ratio was dissolved in Toluene. For preparation of each sample ratio of CNTs and Toluene was kept constant but concentration of Ferrocene was systematically increased. The solution was sonicated ultrasonically at 50 °C and at frequency of 40 KHz for 3 hrs in order to achieve well dispersed CNTs in homogenous solution of Ferrocene and Toluene. The solvent was evaporated at 70 °C and 90 RPM by using Rotary vacuum. A paste of CNTs was achieved and it was dried in Vacuum oven. Same mixture of Ferrocene-CNTs was further calcined in vacuum environment at 200 °C for 3 hrs. After completion of synthesis process few mg of Fe-CNTs composite was put on para film (stretched over petri dish) and it was exposed to Panasonic PE 28S photo camera flash**.** As a result ignition of Fe-CNTs composite was observed. Figure 1 shows the ignition of composite by camera flash.

The synthesized Fe-CNTs Nano composite was characterized by using various analytical techniques. FTIR (Perkin-Elmer) was used to analyse the anchored functional groups on CNTs urfaces. The elemental composition and morphology of the samples were analysed by EDS and FE-SEM (SU 70). TG/DTA (Perkin-Elmer), under nitrogen flow at 50 ml/minute and temperature at rate of 15 °C/min was employed to perform thermal analysis. XRD (Bruker D8 Advance) with Cu K-Alpha radiation was also used to characterize the synthesized composites.

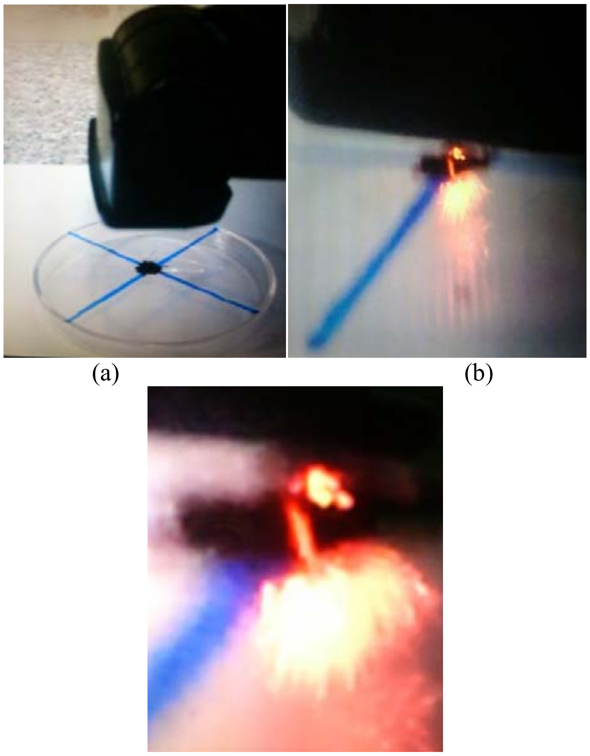


Fig. 1: Image showing Fe-CNTs composite subjected to a camera flash (a), Ignition of the composite by photo flashing (b), Zoom in image of the ignited composite (c).

3. Results and discussion

In order to investigate the growth mechanism of Hydroxyl (OH) and Carboxyl (COOH) functional groups on CNTs surfaces, FTIR spectra of functionalized and pristine CNTs at the mid IR range from 4000 cm^{-1} to 400 cm^{-1} were analysed. Figure 2 shows a strong peak at 3422 cm^{-1} indicates hydroxyl groups and peak at 1636 cm^{-1} shows carbonyl of carboxyl groups on functionalized CNTs surfaces. Similarly a weak Peak at 2920 cm^{-1} shows methylene group (C-H) from a long alkyl chain and the peak at 1429 cm^{-1} is associated with C = C vibration attributed to carbon skeleton. However in the pristine CNTs spectrum there is a relatively weak peak at 3422 cm^{-1} corresponding to hydroxyl group due to moisture and peak at 1629 cm^{-1} shows some residue used in the perpetration of CNTs, which is not available in the spectrum of activated CNTs [13], hence removed via purification and functionalization process.

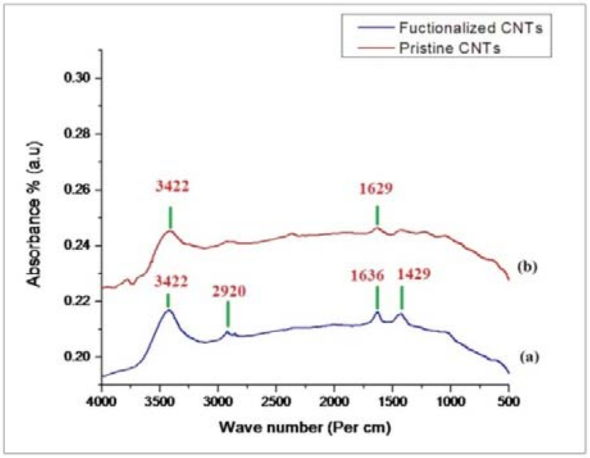
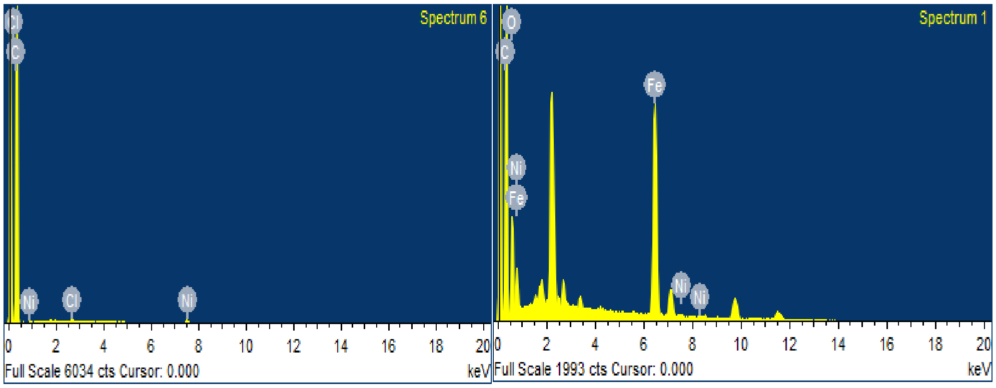


Fig. 2: Image of the FTIR spectra of functionalized CNTs (a) and pristine CNTs (b).

The elemental composition of the composite was analysed by EDS. Table 1 shows that due to purification Ni content reduces to 0.77% by wt from 2.23% and O content increases in functionalized CNTs from 2.04% to 17.73% because of wet oxidation in the result of grafting oxygen containing functional groups on pristine CNTs surfaces. EDS spectra in in figure 3 also ascertain the concentration of Fe particles on the surfaces of activated CNTs. By doping of CNTs with Fe particles some metal Nano particles are adsorbed on the tubes surfaces by reacting with OH and COOH functional groups and convert into FeO, Fe_2O_3 and Fe_3O_4. However some Nano Fe particles adsorb in pure elemental form and these pure Nano particles play the key role to ignite the composite by applying photo flash.

Table 1: Elemental composition of pristine and Fe-CNTs composite.

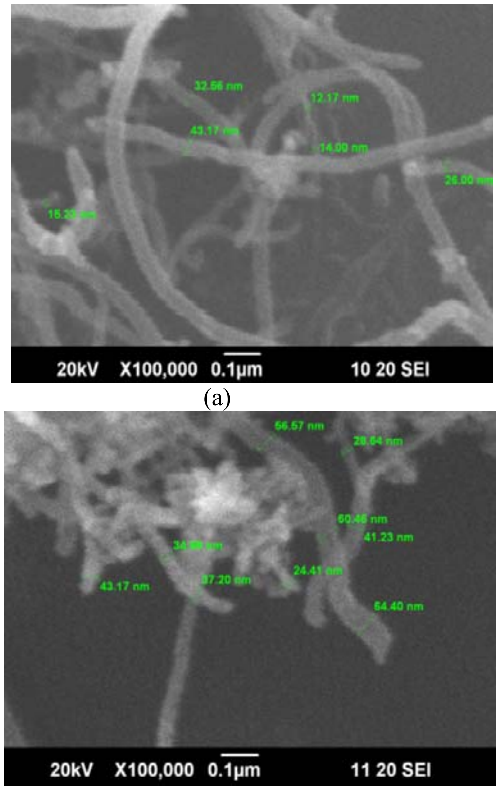
Elements	Pristine CNTs		Fe-CNTs Composite	
	Wt %	**Atomic %**	**Wt %**	**Atomic %**
C K	95.36	97.83	49.29	70.73
O K	2.04	1.57	17.73	19.10
Fe K	-	-	32.22	9.94
Ni K	2.23	0.47	0.77	0.23
Cl k	0.37	0.13	-	-
Total	**100.00**		**100.00**	



(a) (b)

Fig. 3: EDS spectrum of pristine CNTs (a) and Fe-CNTs composite (b).

FE-SEM was used to analyse the morphology of the samples. Following images in the figure 4 show no distortion or defect in CNTs by acid treatment during reflux, at least at the level of SEM images [14]. After functionalization CNTs can be seen well dispersed and very low in impurities. Some changes in the morphology of the CNTs occur due to adsorbed Fe/Fe Oxides particles, the tubes diameters increase and doped CNTs of the composite also get agglomerated.



(a)

(b)

Fig. 4: SEM images of functionalized CNTs (a) and Fe-CNTs composite (b).

TGA was used to determine the role of Fe concentration in decomposition of Fe-CNTs composite. TGA curves under nitrogen environment in figure 5 shows that initially wt of Functionalized/Activated CNTs increases up to 10% due to adsorption of N_2 on CNTs surfaces. Then at 575 ^{o}C their decomposition starts and completes at 700 ^{o}C with 80% wt loss. The wt gain in composite sample with 16% Fe concentration is about 5% up till 350 ^{o}C and from that point onward it begins to degrade with moderate rate till 440 ^{o}C because of the presence of Fe and Fe Oxides particles. Then its rapid degradation starts by oxidation of CNTs and completes at 580 ^{o}C. Similarly the sample with 32% Fe starts losing its wt due to loss of moisture up to 5 % until the temperature reaches at 300 ^{o}C and then at 420 ^{o}C its rapid decomposition starts and completes at 550 ^{o}C with 55 % wt loss. When the same samples were thermally analysed in air environment instead of Nitrogen it was observed that oxidation of the composite occurred at lower temperature [15].

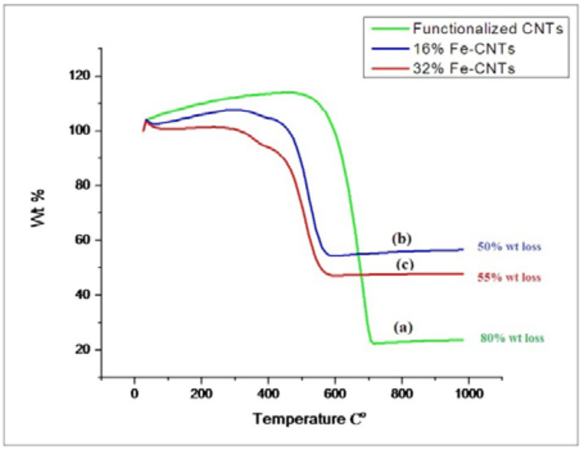


Fig. 5: TGA spectrum showing the decomposition of Functionalized CNTs (a), 16% Fe-CNTs composite (b) and 32% Fe-CNTs composite (c).

Fig. 6 shows XRD patterns for the purified/activated CNTs and Fe-CNTs composites. The pattern of activated CNTs highlights the main, broadened and intense peak at $2\theta = 25.88^{o}$, compared to normal graphite at $2\theta = 26.22^{o}$ and this corresponds to the (002) reflection. The broadening of this peak represents Nano size particles in the structure of CNTs [16]. Rest of the diffraction peaks are at $2\theta = 42.21^{o}$ and 44.36^{o}, indexed to (100) and (101) corresponding to graphite, (JCDPS file no. 01-075-1621) where as 64.41^{o} indexed to (211) reflections, corresponding to Nickel residual crystalline (JCDPS file no. 01-088-1715). The figure also shows a graph of Fe-CNTs composite with 16% Fe concentration and it is obvious from that the diffraction peaks at 25.76^{o} , 44.55^{o} and 64.37^{o} at 2θ get thinned out and strongly reduced in intensity. Similarly in the case of composite with 32% Fe, CNTs are further overlapped by Fe and Fe Oxides Nano particles even till the extent that the peak at 64.37^{o} disappears and intensity of tubes reduces to minimum. This phenomenon can be interpreted that the major peak of Nano tubes at $2\theta = 25.88^{o}$ is completely masked with the peak of Fe/Fe Oxides at 25.76^{o} since these peaks are very close in their positions. Secondly the crystalline extent of Fe/ Fe Oxides is greater than the crystalline extent of CNTs, which leads to the concealing of CNTs peaks. The average crystalline size of Fe particles in the composite is 30.6 nm, calculated by applying Scherer formula.

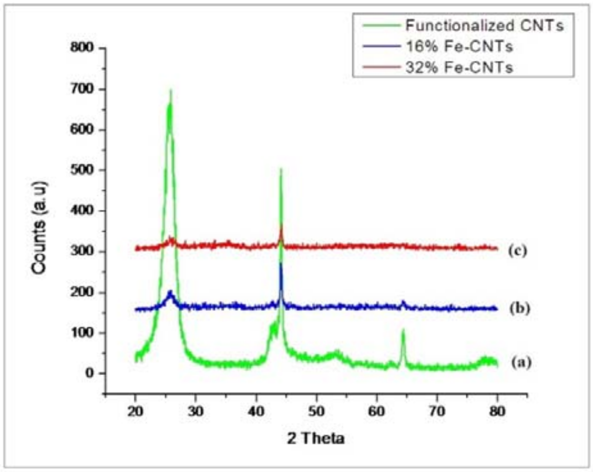


Fig. 6: XRD patterns showing a comparison of purified CNTs (a) with 16% Fe-CNTs composite (b) and 32% Fe-CNTs composite (c).

According to the results discussed above, a synthesis technique of Fe-CNTs composite is proposed. Initially pristine CNTs are purified and activated by wet oxidation as shown in the FTIR results. This process leads to the purification of pristine CNTs by removing amorphous carbon and reducing the content of residual Ni particles to a minimum level. The activation of CNTs also reduces their agglomeration and exposing its maximum surface area for adsorption of Fe particles as shown in FE-SEM images. Nano Fe particles are doped in various ratios and the composite is subjected to camera flashes. It is worth pointing that the ignition of Fe-CNTs composite by camera flash is observed at minimum doping of 16 % Fe by wt whereas maximum ignition efficiency is achieved at 32% Fe by wt. But when these Nano Fe particles are doped in concentration greater than 32 % then agglomeration of CNTs occurs. This reduces the sensitivity of Fe-CNTs composite towards camera flashing. In order to probe out the effect of Fe particles size, Fe powder of 30 micron particle size is also mixed with activated CNTs in different wt ratio, i.e. maximum up to 50% by wt. The mixture is grinded well to obtain homogenous material but no ignition is observed even by applying intensive photo flashes. This implies that only Nano Fe particles in pure elemental form, adsorbed on CNTs surfaces cause the ignition of Fe-CNTs composite by photo flashing. In our case size of the doped Fe particles is 35.5 nm as shown in the above XRD analysis. It is very obvious from TGA analysis that the Functionalized CNTs with no concentration of Fe loses only 5 % wt through out the heat treatment and remain stable up till 600 ^{o}C. Hence Fe concentration makes the CNTs prone to decompose at very low temperature, i.e. at about 400 ^{o}C. Thus it is proven that these Nano metal particles are only impregnated to the surfaces of tubes, where these have their maximum surface area exposed to flashing/heating and air contact for better oxidation.

By further probing the photo flashing effect on Fe-CNTs composites, two phenomena are found to occur when these composites are exposed to camera flash. Firstly, photo energy is absorbed by high content of Nano Fe particles due to black body effect. These Nano particles are oxidized in air and releasing energy in the form of heat. The heat is only dissipated through radial direction of CNTs, being one dimensional in nature. Secondly, Heat dissipation gets slower than heat accumulation. Moreover due to less dense mass of these tubes sufficient amount of heat is accumulated and temperature in the presence of air is elevated to the oxidation point of CNTs. This leads to the ignition of Fe-CNTs composites.

4. Conclusion

CNTs are doped with Nano Fe particles and a composite in the form of Fe-CNTs is synthesised. These doped Nano Fe particles act as hot spots when the composite is exposed to camera flash and its easy ignition is achieved. This causes the composite to release sufficient amount of heat and gas. The synthesised composite can be used as a source of heat and gas which leads to the fabrication of Nano energetic material. The doping technique also holds good for decorating of CNTs with various Nano metals particles, which may be used in many disciplines, e.g. Synthesis of anti pollutant agents.

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[*] Corresponding author: mateen.ec@gmail.com