Facile, soot free approach toward synthesis of carbon nanoropes via chemical vapor deposition of acetylene in the presence of MnFe$_2$O$_4$ coated on stainless steel

Vivek Dhand$^{a,c}$, S. Bharadwaj$^b$, K. Amareshmari$^c$, V. Himabindu$^c$, Kyong Yop Rhee$^{a,}$, Soo-Jin Park$^{d,**}$, David Hui$^e$

$^a$ Department of Mechanical Engineering, College of Engineering, Kyung Hee University, 446–701 Yongin, Republic of Korea
$^b$ Department of Physics, GITAM Institute of Technology, GITAM University, Visakhapatnam 530045, Andhra Pradesh, India
$^c$ Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University, Kukatpally, Hyderabad 500 085, Telangana, India
$^d$ Department of Chemistry, Inha University, Incheon, Republic of Korea
$^e$ University of New Orleans, Department of Mechanical Engineering, New Orleans, LA 70148, United States

**A R T I C L E   I N F O**

**Article history:**
Received 26 June 2015
Received in revised form 13 October 2015
Accepted 28 October 2015
Available online 30 October 2015

**Keywords:**
Carbon nanorope
Chemical vapor deposition
Raman spectroscopy
Manganese ferrite
Super-paramagnetism

**A B S T R A C T**

High density, soot free, novel and a facile approach toward synthesis of carbon nanoropes (CNRs) were successfully carried out in a chemical vapor deposition (CVD) process. Manganese ferrite (MnFe$_2$O$_4$) coated on stainless steel foil (SS 316 grade) was used as a catalyst to initiate the growth of CNR. The coated catalyst was introduced into the CVD and the chamber temperature was set at 700°C later followed with the release of acetylene (50 sccm) and nitrogen (500 sccm) gas, respectively. Total reaction continued until 30 min. No purification or oxidation process of the soot was involved. Analysis reveals the presence of intermingled CNRs with semi crystalline nature of the sample. The elemental analysis confirms the presence of manganese and iron whereas Raman spectrum shows the characteristic narrow G and D bands. The sample displays a super-paramagnetic behavior and is thermally stable up to 500–550°C presenting a strong exothermic reaction.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Since its discovery [1], carbon nanotubes (CNTs) have sparked an intense curiosity among researchers for its unique microstructure and excellent physical and electrical properties. It is due to these properties, the CNTs find their way into several applications [2]. Until now, several synthesis methodologies have been devised for the production of CNTs which includes arc discharge [3], flame synthesis [4], laser ablation [5] and chemical vapor deposition [6]. Of these processes, CVD has shown promising results in the production of CNTs. Moreover CVD process has an added advantage over others due to the high yield, high purity and selective growth in the production of CNTs. [7–9], the same approach may also be utilized for the production of carbon nanoropes (CNRs) [10]. Several researchers have reported the dependency of the structure of carbon nanomaterials based on the synthesis parameters like reaction time, gas feed, temperature and catalyst composition, respectively [11–13]. By fulfilling all these prerequisite conditions, the design and structure of the carbon material (CNRs in this case) can be exploited. The prominent and determining factor for the controlled CNRs growth is the maintenance of the uniform temperature and the catalyst activity during the reaction [10,14,15]. Presence of any undesirable carbonaceous byproduct is always a major hindrance in the growth and yield of the CNRs produced using the above mentioned methods even under the controlled conditions. Fundamentally, the as-produced CNRs mixture requires expensive, tedious and an inefficient procedure for the purification. To assuage this problem, several catalytic research towards the soot free synthesis have been carried out but still few problems of the unwanted soot persists [16–18]. Moreover, during the peak decomposition process within the heart of the CVD chamber, the re-arrangement of the bond structure in carbon develops continuous loss of non-carbon species from the feedstock (reactants) leading to its complete breakdown and formation of soot. The main decisive factor between the formation of soot and the CNRs is the residence time period and the feasible energetic rearrangement of the carbon bonds during the reaction. In other words, soot is produced more often when there is a lack of adequate residence time for the carbon structure to rearrange itself [19]. Hence a complete
catalytic activity and transformation of the carbon feed stock into the desired nanomaterial for prospective applications with high purity and yield is the need of an hour. In general, a nanotube is a single cylindrical structure which is either composed of a single wall (SW) or a multiple walled (MW) graphene layers. Whereas a nanorope is formed in-situ when a group of several graphene layers of nanotubes (SW or MWNT) are coiled or braided due to the chamber heat and reaction conditions to form a composite yarn like structure. Several morphological observations as seen under SEM and TEM, points out to the cylindrical structure of the rope that is composed of several multilayers and is highly coiled internally which “mimics” the rope like structure. When we compare it with chemical composition and morphological makeup, on structural and functional (application) basis, we assume that the CNT is an individual unit of a CNR, with no major difference between them. Hence the etymology of carbon nanoropes was employed in the present study.

As far as the knowledge of authors go, very few researchers have so far reported the in-situ mode of CNR synthesis involving several parameters like addition of ammonia gas, pretreatment of SS substrate with acid or inert gas, and at higher temperatures [2,10,12]. However, till date several ferrites have been employed for the synthesis of nano carbons via CVD process, but so far no report has been observed on catalytic activity of MnFe2O4 forCNT or CNR synthesis via CVD approach. So far several attempts have also been made to synthesize it without soot. And several authors have always reported the presence of good amounts of soot which further requires a tedious purification procedure. The following section attempts to understand the trend in different catalytic approaches adopted by various researchers to produce soot free nanoproducts. Earlier, Rodgers et al. reported a similar viewpoint when they synthesized soot free fullerences from acetylene pyrolysis under similar conditions, where they reported that the presence of soot occurs only when the temperature is raised to or beyond 800 °C, but when the temperature is around or below 700 °C, they observed pure fullerences devoid of any soot matter. Apart from this they also reported that the presence of metallic catalyst at 700 °C can produce CNTs with high yields [19]. They also discussed that due to the lack of dangling bonds, fullerene material like CNTs, CNR, C60 etc., are more thermodynamically stable than that of the soot [19,20]. Nevertheless, earlier to Rodgers, Schilltler et al. synthesized single crystals of nano carbon rods with uniform length and diameter by thermolysis of C60 and nickel nano-patterned as layers on a molybdenum surface [21]. Teng et al. [22], demonstrated that with the use of Ni-dots as a catalyst, in the presence of CH4 or C2H2 gases, the CNTs synthesized by CVD were bearing traces of soot (but in our case the catalyst used was devoid of Ni and the participation of Ni from SS foil is also not accountable since it wasn’t detected in EDXRA). Whereas when the catalytic conversion of the nanodiamonds into CNTs was carried out they did not observe the presence of any soot material, respectively. Ran et al. [23], doped Mn on a NiMgO substrate to synthesize CNTs using CVD, they found that Mn acts as a promoter for synthesis of good yields of CNTs devoid of any amorphous phases of soot. Akbarnejad et al. [24], demonstrated the catalytic activity of spinel ferrites [cobber ferrite (CuFe2O4), (ii) ferrite where cobalt is replaced by nickel (Ni1Co1−xFexO4, where x = 0, 0.2, 0.4, 0.6), and (iii) ferrite where nickel is replaced by zinc (Zn1Ni1−xFexO4 where y = 1, 0.7, 0.5, 0.3), for synthesizing CNTs using CVD. The results obtained did show some amorphous carbon, but the authors did not specify much detail on it except that the sample was purified by air oxidation at 400 °C. Recently, Bacsca et al. [25], demonstrated the synthesis of few layer graphene (FLG) and carbon nanofibers (CNFs) using transitional metal ferrites where they showed that the CNFs in high yields could be synthesized using CoFe2O4 as a catalyst at low temperatures up to 450 °C and high yields of FLG between 620 and 720 °C, respectively. Even they have also not reported anything on purification and presence of soot during synthesis. Taking into few of these accounts we report for the first time the catalytic activity of MnFe2O4 as an efficient catalyst, drop casted on stainless steel substrate for the synthesis of soot free CNR/CNTs and other nanocarbons using CVD. CNRs were synthesized in high densities by using CVD at 700 °C. A thin slurry paste (≤0.05 g) of MnFe2O4 as the catalyst was drop casted on the 0.1 mm thick stainless steel foil. The carbon sample obtained shows extremely long, spirally coiled and intermingled CNRs with diameters around 20–150 nm. The as-prepared sample is completely devoid of amorphous carbon and contains only CNRs enveloping the ferrite particles. Further there was no need for purification.

2. Experimental materials and methods

All the chemical reagents like Citric acid, Fe(NO3)3.9(H2O) and Mn(NO3)2.6(H2O) were purchased from Sigma Aldrich and were further used without any purification. SS316 grade stainless steel foil of 0.1 mm thickness was purchased from a local Indian steel market.

2.1. Experimental

2.1.1. Ferrite synthesis

The MnFe2O4 was synthesized using a solution combustion technique, where a stoichiometric ratio of Fe(NO3)3.9(H2O) and Mn(NO3)2.6(H2O) were dissolved in the double distilled water. Citric acid was then added to the above mixture thereby maintaining the acid/metal at 1:1 molar (M) ratio, respectively. The mixed solution was then placed in a furnace maintained at 450 °C, which resulted in auto ignition and finally yielded the MnFe2O4 as a black powder. The as-prepared ferrite powder was then sintered at 800 °C for 1 h to remove any carbonaceous residue from citric acid. The slurry of MnFe2O4 was prepared using very small amounts of double distilled water. The thick slurry paste (≤0.05 g) was drop casted, spread and dried on the 2 cm × 5 cm SS 316 grade foil (thickness of 0.1 mm). The dried coating was then introduced into the center of the CVD chamber (Fig. 1).

2.1.2. CNRs synthesis

CNRs synthesis was carried out under atmospheric conditions. The chamber temperature was set at 700 °C and the flow rates of acetylene and nitrogen were set at 50 sccm and 500 sccm, respectively. The reaction continued for 30 min, after the completion of the experiment the chamber was allowed to cool slowly to room temperature in the presence of nitrogen gas. After the cooling, the quartz tube was then cleaned to obtain the carbonaceous material collected around the tube and on the SS foil. No purification steps were undertaken. The as-received sample was further analyzed for its crystallinity, morphology, quality thermal stability and magnetic property.

3. Results and discussion

3.1. X-ray diffraction (XRD) studies

Fig. 2 shows the XRD (Bruker AXS-D-8 Discover) pattern of the sample with a strong peak of (0.02) graphite at 2θ angle of 26.2° (JCPDS no. 75-1621) and small signal of (1 0 1) graphite at 44.6° (JCPDS no. 25-0284), respectively. The small signals at 2θ angles of 35.0°, 40.6°, 42.9°, 45.1°, 58.9° with lattice plane orientations of (3 1 1), (4 1 1), (0 2 4), (3 3 2) and (6 0 0), respectively corresponds to the presence of cubic manganese ferrite atoms (JCPDS no. 10-0319) and (JCPDS no. 71-0637) [26]. The sample also exhibits semi
crystalline phase as observed in the diffractogram. The sample scan also displays that the fingerprint broadened amorphous soot phase between 2θ angles of 10.0° and 25.0° is also absent thus inferring that the synthesized product is almost soot free. Using Scherer’s formula the crystallite size for the peaks displaying (002), (311), (411), (024), (332) and (600) were calculated [27]. The results show that the crystallite size for these peaks are around 17.5 nm (002), 53.4 nm (311), 54.3 nm (411), 31 nm (024), 19 nm (332) and 16 nm (600), respectively. Based on the crystallite size data, it may be noted that the diameter of the rope is purely dependent on the size of the catalyst particle, where several reports have already shown that any particle with range beyond 15–20 nm may result in the production of thick walled carbon nanoropes, respectively [28–30].

3.2. Scanning electron microscope analysis

The SEM image (FE-SEM: LEO SUPRA 55, Carl Zeiss, Germany and HR FE-SEM MERLIN Carl Zeiss) shows densely grown extremely long, almost soot free, highly intertwined and continuous nanoropes with variable diameters (Fig. 3a–c). The diameter of thick nanoropes is between 150 and 300 nm whereas the smaller nanoropes range between 90 and 150 nm, respectively. The thicker ropes are obtained due to the saturation or unavailability of catalyst with the carbon seed and therefore the control of diameter could not be possible which resulted in the growth of thicker ropes [13–15]. The elemental composition (Fig. 3d) of the sample shows the presence of Mn, Fe, C and O in the EDAX confirming the presence of catalyst in trace amounts. Few more focus points of the as prepared samples are shown in Fig. 3(e–j), which were obtained using HR FESEM equipment, where the scan clearly shows the presence of similar types of nanoropes with variable diameters within the sample. As one can also observe, that the smaller ropes are highly intertwined, whereas the bigger ropes are long and are fused together all throughout their sides. A very small globose type of beaded carbon sphere can be seen which terminated abruptly before forming into a rope. This instance has been found only once within the sample. As observed the globose sphere is parallel acting as a template for the growth of ropes on its surface (Fig. 3f). On further magnification we can also observe that the spheres fuse to form a rope due to Oswald’s ripening effect which makes the surface more even and smooth there by removing the fused joints of the spheres as observed in (Fig. 3i and j). Based on these observations, we can demonstrate the fact that the catalyst poisoning occurs spontaneously for the smallest particle as the carbon-flux increases rapidly across its surface. Since the flux is dependent upon the surface to volume ratio of the particle, the catalyst gets poisoned and results in the formation of thinner nanoropes [31]. On contrary to this, when the flux is too high, the catalyst particle keeps attracting the carbon onto its surface which results in the formation of several closed packed and denatured external layers of carbon walls and independent, spheres which later fuse together and leads to the growth of larger diameter nanoropes as observed in the present study [31].

3.3. High resolution transmission electron microscope analysis

TEM (JEM2100F-JOEL) images are shown in Fig. 4a–b. The images show intermingled ropes of diameter between 90 and 300 nm along with the presence of small internal dark cubic catalyst patches measuring approximately 50 nm, respectively. Presence of thick walled nanoropes can also be seen but their numbers are very few as compared to the thin walled nanoropes. A higher resolution image (Fig. 4c) shows the multi layered walls (~20–30 layers) of nanorope covering the catalyst (dark black body inside) leading to the encapsulation as observed. This insertion could be attributed to
Fig. 3. (a–c) FE-SEM images of MnFe$_2$O$_4$ catalyzed CNRs; (e–j) HR FE-SEM images of various focus points of the MnFe$_2$O$_4$ catalyzed CNRs (d) EDAX pattern of MnFe$_2$O$_4$ catalyzed CNRs. Scale bar: (a) 100 nm; (b) 1 μm; (c) 100 nm; (e) 2 μm; (f) 200 nm (g) 2 μm; (h) 1 μm; (i) 100 nm; (j) 100 nm.
the weak interaction between the catalyst and the seeding carbon droplet formed during the reaction which covered the catalyst completely [32]. The SAED pattern (Fig. 4d) shows nano-polycrystalline nature of the catalyzed ropes with the presence of bright spots along the rings. Similar patterns are observed for several focus points in the sample, thus inferring the uniform distribution of the particles within the sample.

3.4. Raman spectroscopy

Fig. 5 depicts the Raman spectrum (inVia Raman) of the sample obtained using a 514 nm argon ion laser. The sample exhibits the characteristic fingerprint zones of a carbon material. The total scan was measured between the wavenumbers of 3200–100 cm⁻¹, respectively. The analysis was carried out using half the laser power (50 mW) to resolve the peaks well. The sample scan shows the presence of slightly broader D-band (1345 cm⁻¹) and extremely narrow G-band (1597 cm⁻¹) which infers the presence of higher degree of graphitization but with defects [33–36]. This is caused due to the growth of thick nanoropes which resulted in the saturation or unavailability of the catalyst which have several layers of distorted SP2 graphene walls along the c-axis. As observed from TEM, there are several ropes which are spirally intermingled and have distorted layers. Based on the function of the intensity ratio of the D and G bands (I_D/I_G = 1.01) it was found that the material is indeed having several layers of graphene walls closely packed together, which increases the rope diameter and decreases the functionality of the material [37]. On further scanning one can observe a faint composite protrusion between the wavenumbers of 3000–2500 cm⁻¹, respectively. This feature is generally attributed to the presence of a characteristic 2D(G') band graphitic carbon which is composed of highly condensed and compact helical layers.
Thermo-gravimetric and differential thermal analysis

Thermo-gravimetric studies (GA Q5000 IR/SDT Q600 (TA) of the sample (Fig. 6) was carried out in the presence of air to assess its stability at high temperature. All the TGA measurements were executed until complete oxidation of the sample was achieved. The thermogram shows that the sample was stable up to 500–550 °C without losing any mass. The temperature displayed by the DTA peak ascertains the stability of the CNRs. Higher the temperature region of the DTA peak, better is the stability of the sample [39]. This is due to the fact that the highly stable CNRs can withstand higher oxidative temperatures during the TGA experiment. As observed in our case, several CNRs displays well graphitized walls with medium crystallinity; hence they are able to withstand intermediate temperatures between 500 and 550 °C [40]. But as the temperature increases one can observe a strong exothermic reaction involving the degeneration of the outer graphene layers of the rope. The absence of a stepwise drop between 200 and 400 °C infers that the sample is completely devoid of soot/amorphous phases of carbon, since several reports suggests that if there is any presence of soot within the sample the thermograms displays a step wise descent representing degradation of sooty material within the temperature ranges of 200–400 °C [41–45]. When the temperature reaches around 620 °C the total weight loss at this junction is about 93.45% amounting to the complete oxidation of the carbon nanoropes. The oxidized catalyst content in the CNRs can also be measured from the residual weight obtained after the complete oxidation of the total sample during the thermal analysis [46,47]. In our case the sample was found to contain 6% of the total mass of the CNRs sample. The remaining residue was re-analyzed for its composition, it is attributed to the presence of the oxidized manganese ferrite particles as observed from the EDAX results.

3.6. Vibrating sample magnetometer (VSM)

The magnetic property of the CNR-MnFe₂O₄ sample was investigated at room temperature by a Vibrating Sample Magnetometer (VSM) up to a magnetic field of 15kOe. Fig. 7 shows that the sample synthesized is super-paramagnetic in nature. The saturation magnetization for the sample is 3.34 emu/g. The low value of saturation magnetization is due to presence of carbon nanoropes which are enveloping the ferrite particle caused during the chemical deposition method. The presence of narrowness in the band of the loop is also attributed to the enveloping effect caused due to the graphite layers and its distortions within the nanoropes. Similarly, Liy et al. explained that the presence of a nanocarbon (CNR in our case) leads to the structural deformation of the ferrite structure in which interaction between the oxygen and metal ions increases leading to decrease in the magnetic moment of the sample [48]. A similar reduction of magnetization in ferrite-CNT based samples was found by various researchers [49,50]. The figure also shows that the sample got saturated at a very high field of 15kOe which may be due to lower particle size of ferrite or presence of CNR envelope. The particle sizes of the ferrite as calculated by TEM and also XRD (at various peaks) are in agreement with pattern of the magnetic hysteresis loop. As reported earlier by several authors, any particle size <50 nm (~5 nm) would display a super-paramagnetic behavior with lower values of coercivity and remanence [51,52]. Another determining factor responsible for the super-paramagnetism in our sample may be attributed to the spin canting and surface spin disorder within the ferrite with lower dimensions [53]. Hysteresis loops for the sample had displayed very low coercivity and remanence, expecting a super magnetic behavior. Based on these findings, this behavior may be useful...
3.7. Effect of catalyst and steel

A very important parameter for control of the CNR diameter during the nucleation process is extremely dependent upon the size of the catalyst. It has been reported earlier by several researchers that any catalyst particles with size less than 4–5 nm helps in the production of single-walled carbon nanotubes (SWNTs), while the particles with diameters greater than 15–20 nm results majorly in the production of thick multiwalled carbon nanotubes (MWCNTs) [28–30]. It is only during the phase change of the ferrite (ferrite to lower oxides) where the catalyst is much more in an active form, during the synthesis within the chamber. The effect of increasing temperature results in the calcination of the ferrite leading to the formation of the metal oxides and later carbon nanotubes when the C_{2}H_{2} is released which later results in variable morphologies like thin, thick coiled ropes as shown in Figs. 3 and 4. As observed from the TEM images, catalyst particle also agglomerates at several places with ropes following a tip growth pattern [54]. On the other hand, steel plays an important role in the synthesis of CNRs [55–59]. Several reports suggest that during the pre-growth initiation phase, CNRs selectively pulls out iron from the steel, thereby excluding other metallic species (Ni, Cr, Mo etc.) from the alloy surface. So it’s a well-known fact that, iron in austenitic steel exists in a γ-phase due to the presence of a stabilizer in the form of nickel within the alloy. Therefore during the nucleation/seedling/initiation process of CNRs, the iron from the catalyst and steel synergistically helps in the formation of CNRs The formation of an iron carbide phase on the outer layers of the catalyst nanoparticle represents the proto-stage for the growth of CNRs [60–63]. Apart from the chemical parameters, the effect of temperature adds up to the contributing parameters for the development of CNRs. Few reports have already suggested that the growth of CNRs in the presence of iron catalyst and lower alkanes (CH_{4}, C_{2}H_{4}) directly affects the dimensions (diameter and length) of the CNRs during the growth process. Once the saturation point reaches due to the catalyst poisoning caused by the excess carbon flux, Ostwald’s ripening takes effect and detaches the nanoropes away from the catalyst/substrate [64–67].

4. Conclusions

An efficient approach has been demonstrated for soot free synthesis of high density CNRs using MnFe_{2}O_{4} coated on SS316 foil in CVD. It is known that the soot free synthesis is a real challenge for the high rate production of CNRs. Since several parameters are involved in the growth of CNRs, one cannot omit the importance of the catalyst and its activity. The process has shown that 700 °C is an effective temperature and MnFe_{2}O_{4} a promising catalyst for synthesizing soot free CNR’s using CVD. The results also infer that the catalyst is helpful in the control of rope diameter and enhances the quantity of the CNR produced herein. If there is an insufficient supply of catalyst due to saturation or exhaustion of the seed particle, the formation of thicker nanoropes with low crystallinity and higher wall deformities are observed thereby decreasing not only the yield (quantity in this case) but also the quality. The super-paramagnetic nature of the sample in future may also help us open new possibilities in magnetic sensitivity application along with manipulation of magnetic integrated systems in a biomedical field.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Project Number: 2013R1A1A2A01063466).

References


