Synthesis of nano-carbon (nanotubes, nanofibres, graphene) materials

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Abstract. In the present study, we report the synthesis of carbon nanotubes (CNTs) using a new natural precursor: castor oil. The CNTs were synthesized by spray pyrolysis of castor oil–ferrocene solution at 850°C under an Ar atmosphere. We also report the synthesis of carbon nitrogen (C–N) nanotubes using castor oil–ferrocene–ammonia precursor. The as-grown CNTs and C–N nanotubes were characterized through scanning and transmission electron microscopic techniques. Graphitic nanofibres (GNFs) were synthesized by thermal decomposition of acetylene (C_2H_2) gas using Ni catalyst at 600°C. As-grown GNFs reveal both planar and helical morphology. We have investigated the structural and electrical properties of multi-walled CNTs (MWNTs)–polymer (polyacrylamide (PAM)) composites. The MWNTs–PAM composites were prepared using as purified, with ball milling and functionalized MWNTs by solution cast technique and characterized through SEM. A comparative study has been made on the electrical property of these MWNTs–PAM composites with different MWNTs loadings. It is shown that the ball milling and functionalization of MWNTs improves the dispersion of MWNTs into the polymer matrix. Enhanced electrical conductivity was observed for the MWNTs–PAM composites. Graphene samples were prepared by thermal exfoliation of graphite oxide. XRD analysis confirms the formation of graphene.

Keywords. Carbon nanotube; graphitic nanofibres; graphene; CNTs–polymer composite; polyacrylamide.

1. Introduction

In the emerging field of nanomaterials, carbon nanostructures have potential significance. The various categories of carbon nanostructures include fullerenes, carbon nanotubes (CNTs), graphitic nanofibres (GNFs), graphene, etc. Carbon nanotubes (CNTs) have outstanding electrical, thermal and mechanical properties which make them interesting material for applications in nanoelectronics, sensors, field emission and as reinforcing agents in composite materials (Terrones 2003). The most important methods developed to produce CNTs include electric arc discharge (Ebbesen and Ajayan 1992), laser ablation (Thess *et al* 1996), and chemical vapor deposition (CVD) (Colomer *et al* 2000; Awasthi *et al* 2003). In any industrial application, an important issue in the production is the cost, quality, and yield of CNTs. The CVD method (in which hydrocarbon is pyrolyzed in the presence of transition metal catalysts) has attracted attention due to possibility to produce nanotubes on a commercial scale. Till date, several precursors such as carbon monoxide, methane, acetylene, benzene, xylene, etc have been used

as a carbon feedstock to synthesize CNTs (Srivastava *et al* 2004). These precursors are related to fossil fuels and they may be crisis for these precursors in near future. There are few reports on the synthesis of CNTs from natural precursors e.g. turpentine, eucalyptus oil and camphor (Afre *et al* 2006; Kumar and Ando 2005; Ghosh *et al* 2007). The advantages of using natural precursor as a carbon feedstock for synthesizing CNTs is that it is inexpensive and there is no chance of shortage in near future. Doping CNTs with heteroatom could be particularly an interesting way for tuning the surface and electronic properties. Incorporation of nitrogen in CNTs results in the enhancement of conductivity, due to the additional electron contributed by the nitrogen atom (Glerup *et al* 2003). The nitrogen containing carbon (C–N) nanotubes are effective field emitters.

CNTs based nanocomposites are increasingly being reviewed as a realistic alternative to conventional smart materials, as they offer higher sensitivity and superior electronic properties. The CNTs are expected to reinforce their unique properties to the polymer matrix with many further applications (Castro *et al* 2009). A number of research efforts have been used for polymer composites reinforcement (Awasthi *et al* 2006; Singh *et al* 2008). The optical and electrical properties of the poly

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(3-hexylthiophene) – SWNTs composites have been studied and an increase of ~ 5 orders of magnitude in electrical conductivity was observed for a 30 wt% concentration of SWNTs in polymer matrix (Singh *et al* 2008). But there are still many practical challenges in the preparation methods due to the agglomeration of CNTs. In order to optimally utilize the CNTs as a reinforcing component in the polymer matrix, some special treatments of CNTs, such as physical or chemical treatments are used to achieve better CNT dispersion and good interface between CNTs and polymer matrix (Moniruzzaman and Winey 2006). Physical methods involve ultrasonication, milling to physically separate the tubes that are bundled together. Chemical methods involve use of surfactant or chemical functionalization of the tube surface which improves interfacial bonding between the nanotubes and polymer and can prevent the tube aggregation. Several groups have studied the electrical and mechanical properties of CNTs–polymer composites using physically/chemically treated CNTs (Ma *et al* 2007; Kim *et al* 2008). In our earlier study, we have prepared multiwalled CNTs (MWNTs)–polyethylene oxide (PEO) composites and studied their electrical and mechanical properties (Awasthi *et al* 2006). Enhanced electrical conductivity and mechanical strength were observed for the MWNTs–PEO composites.

In other carbon nano materials such as graphite nanofibres (GNFs) graphitic sheets are parallel, perpendicular or inclined. Since the advent of GNFs (Baker *et al* 1972), they are being studied in depth due to their unique structure, distinctive physical and chemical properties and several feasible applications. GNFs can be used as reinforcement materials, battery components, polymer additives, fuel cell electrodes, nanoelectronics, hydrogen storage, novel catalyst, etc (De Jong and Gues 2000; Serp *et al* 2003; Nakayama 2004). GNFs are prepared by pyrolysing hydrocarbon compounds in the presence of transition metal particles like Ni, Co, Fe and alloys of these metal particles. The growth of GNFs has been achieved by employing carbon containing gases such as CH_4 , C_2H_6 , C_2H_2 , C_2H_4 , CO, etc used as feedstock. One exotic structure of the GNFs is its helical (coil) form known as helical graphitic (carbon) nano fibres. Carbon nanocoils have been synthesized (Pan *et al* 2002) by catalytic pyrolysis of acetylene using iron-coated indium tin oxide as catalyst. In this communication, we report synthesis of GNFs by employing fine particle of Cu–Ni as catalyst.

New carbon materials such as graphene discovered recently are automatically thin sheets of carbon atoms tightly packed in a two dimensional honeycomb lattice, possessing many extraordinary properties, whose potential applications have recently been the subject of intense scientific interest (Geim and Novoselov 2007). The first historical isolation of single-layer graphene from the crystalline graphite was demonstrated by Novoselov *et al* (2004). Graphene exhibits fascinating properties such as

quantum Hall effect at room temperature, ballistic conduction with high mean free path, tunable band gap, and high elasticity. Chemical and other properties of graphene also seem to be fascinating. Polymer composites based on graphene are expected to show interesting electronic and mechanical properties (Stankovich *et al* 2006). However, obtaining a single sheet of graphene is a challenge. Graphene was generally prepared by micromechanical cleavage of highly oriented pyrolytic graphite (HOPG) (Novoselov *et al* 2004). This method cannot be employed for large scale production or to study many of the chemical and mechanical properties of graphene. Various types of graphene samples have been prepared by chemical vapour deposition (Reina *et al* 2009), arc evaporation of SiC (Li *et al* 2001), and exfoliation of graphite oxide (GO) (Schniepp *et al* 2003). Recently, graphene sheets were prepared by arc evaporation of graphite rod under hydrogen and argon atmosphere (Subrahmanyam *et al* 2009). More recently, graphene sheets (nanoribbons) were prepared by chemical oxidation of CNTs (Kosynkin *et al* 2009).

In the present study, we report the synthesis of CNTs/C–N nanotubes by spray pyrolysis, graphitic nanofibres by catalytic thermal decomposition of hydrocarbon gas such as C_2H_2 . In addition, we also report the preparation of CNTs–polyacrylamide (PAM) composite films by solution cast technique by using as-purified, ball milled and functionalized MWNTs and synthesis of graphene sheets by thermal exfoliation of graphite oxide.

2. Experimental

2.1 Synthesis of carbon/carbon–nitrogen (C–N) nanotubes

Synthesis of CNTs was carried out using spray pyrolysis assisted CVD method. We used ferrocene ($\text{C}_{10}\text{H}_{10}\text{Fe}$) as a source of iron (Fe) which acts as a catalyst for the growth of CNTs. Castor oil was used as the carbon source. Castor oil contains carbon, hydrogen and lower amount of oxygen. The spray pyrolysis setup consisted of a nozzle (inner diameter ~ 0.5 mm) attached to a ferrocene-castor oil supply used for releasing the solution into a quartz tube (700 mm long and inner diameter 25 mm), which was mounted inside a reaction furnace (300 mm long) (Srivastava *et al* 2004). The precursor solution i.e. ferrocene with castor oil (concentration ~ 25 mg/ml) was sprayed through the nozzle into the pre-heated (850°C) quartz tube, using Ar as carrier gas. The optimum flow rate of Ar was ~ 100 sccm (standard cubic centimeter per minute). The precursor solution was sprayed for 15 min at a constant flow rate of ~ 0.5 ml/min. For C–N nanotubes instead of castor oil and ferrocene solution, solution of castor oil-ferrocene with liquid ammonia (NH_3) was used. Ammonia was used to obtain native source of

nitrogen in the precursor. The optimum ratio of castor oil to ammonia was 15 : 1 (volume wise). For this solution, the optimum ferrocene concentration was 20 mg/ml. After deposition, the furnace was put off and allowed to cool down to room temperature under Ar gas flow. A black deposit was extracted from the reaction zone (center of the furnace) of quartz tube.

2.2 Synthesis of graphitic nanofibres

In the present investigation, GNFs were grown by using catalytic thermal decomposition of hydrocarbon gas such as C_2H_2 . The C_2H_2 was prepared through the inexpensive process by employing calcium carbide (CaC_2) stone and water. Detailed description of the synthesis of GNFs are described in our previous publication (Singh *et al* 2004). Briefly, 100 mg of Ni (96%) and Cu (4%) were taken for each run of the GNFs synthesis, since it was optimum for our experimental setup.

2.3 Synthesis of CNTs-polymer (polyacrylamide) composites

The MWNTs were functionalized with amino group via chemical modification of carboxylic groups introduced on the nanotube surface. This process involves a direct coupling of ethylenediamine with carboxylic groups to introduce amino groups via amide formation (Ramathan *et al* 2005). The MWNTs-PAM composites were prepared by the solution cast technique using as-purified, ball-milled and functionalized CNTs. The details of the MWNTs-PAM composite preparation method is given in our previous publication. The PAM powder (BDH Chem. Ltd, Molecular weight $\sim 5 \times 10^6$) was dissolved in 50 ml distilled water and mixed with MWNTs at different wt% (5, 15, 20, 25, 30 and 40 (Awasthi *et al* 2009).

2.4 Synthesis of graphene

Graphite oxide (GO) was prepared by reacting graphite powder (5 g) with a mixture of conc. nitric acid (45 ml) and sulphuric acid (90 ml) with potassium chlorate (~ 55 g) at room temperature for 5 days. For thermal exfoliation of graphite oxide, the dried graphite oxide powder (~ 200 m) was placed in a quartz tube (diameter ~ 25 mm and length ~ 1.3 m). The sample was flushed with Ar for 15 min and the quartz tube was quickly inserted into a furnace preheated to 1050°C and held in the furnace for 30 s. The as-prepared GO was a brownish powder while the exfoliated version was of light consistency and shiny black.

The structural characterization of all the carbon nano materials were carried out using X-ray diffraction technique employing X'Pert PRO PANalytical diffractometer equipped with graphite monochromator with a Cu

source ($\lambda = 1.54 \text{ \AA}$, $\text{CuK}\alpha$ operating at 45 kV and 40 mA). The as-grown carbonaceous material was characterized by using scanning (SEM, Philips XL 20), and transmission (TEM, Tecnai 20 G^2) electron microscopes.

3. Results and discussion

3.1 Carbon/carbon-nitrogen (C-N) nanotubes

Spray pyrolysis of castor oil-ferrocene solution at $\sim 850^\circ\text{C}$ in Ar atmosphere leads to a uniform thick black deposition on the inner wall of the quartz tube at the reaction hot zone ($\sim 850^\circ\text{C}$). Figure 1a shows the SEM morphology of the as-grown CNTs. The length of CNTs is $\sim 5\text{--}10 \mu\text{m}$. Structural details of the as-grown CNTs sample was further investigated by TEM. Typical TEM image of the as-grown CNTs is shown in Figure 1b. The TEM investigation of as-grown CNTs confirms that the CNTs are multi-walled in nature. These nanotubes have varying diameters ranging from $\sim 20\text{--}60$ nm. In the spray pyrolysis reaction, the castor oil-ferrocene solution was atomized via spray nozzle and sprayed through carrier gas (Ar). The Fe particles (liberated by the decomposition of ferrocene) were deposited on the inner walls of the quartz tube. The carbon species released from decomposition of castor oil and also from ferrocene got adsorbed on the Fe particles and diffused rapidly along the axial direction leading to the formation of CNTs.

In the present study we also used castor oil-ferrocene with ammonia solution so as to develop CNTs containing nitrogen i.e. C-N nanotubes. This was done keeping in view the fact that nitrogen doped CNTs are considered as one of the important ingredients of CNT based electronics. Figure 2a shows a typical SEM micrograph of as-grown C-N nanotubes, which reveals the wavy morphology of nanotubes. These wavy nanotubes are most likely due to pentagonal and heptagonal defects that are introduced in the hexagonal sheets. TEM images of the as-grown C-N nanotubes are shown in figure 2b. These CNTs have bamboo-shaped structures. The TEM image (figure 2b) shows that the nanotubes have a range of diameters varying from $\sim 50\text{--}80$ nm. It is suggested that the bamboo-shaped morphologies arise from the incorporation of pyridine-like N atoms within the carbon framework (Nath *et al* 2000; Lee *et al* 2002). Also, no encapsulated metal particle was found inside the nanotubes. The tip of CNT is generally covered by catalyst particles.

3.2 Graphitic nanofibres

Average particle size of as-used Cu-Ni catalyst was about $12 \mu\text{m}$ measured by particle size analyzer which was also

Figure 1. SEM (a) and TEM (b) micrographs of the as-grown CNTs obtained by spray pyrolysis of castor oil–ferrocene solution at $\sim 850^{\circ}\text{C}$.

Figure 2. SEM (a) and TEM (b) micrographs of the as-grown C–N nanotubes obtained by spray pyrolysis of castor oil–ferrocene with ammonia solution at $\sim 850^{\circ}\text{C}$.

confirmed by TEM images. However, in the as-grown GNFs samples the size of the catalyst particles was in nanometer (~ 150 nm) range which confirmed that at the time of GNFs synthesis these catalyst particles were broken into finer particles. After the growth of graphitic nanofibres, the as-synthesized product which also contained the catalyst particle was characterized through XRD. Analysis of the XRD pattern revealed the dominant presence of graphitic nano phase (crystallite size 3.6 nm) together with nickel. The observed d spacing of the GNFs was ~ 0.342 nm which is very close to the ideal d value of graphite ~ 0.335 nm. This shows that quite good graphitic nature is maintained for the synthesized GNFs. TEM micrographs shows that GNFs were synthesized successfully (figure 3). It was observed that at synthesis temperature 600°C the as-synthesized GNFs were in planar form (figure 3a). However, at synthesis temperature of 700°C the GNFs were in helical form (figure 3b). TEM explorations revealed that the Ni particle size associated with

GNF growth is ~ 150 nm and also that it was equivalent to the diameter of the GNFs. Length of these GNFs were in the range of $6\text{--}8\text{ }\mu\text{m}$ and the average diameter was ~ 150 nm.

It was observed that the morphology of the GNFs depend on the synthesis temperature. In the present investigation we have obtained both planar and helical morphology by using Cu–Ni catalyst but at different temperature. Temperature is an important parameter which decides the catalyst shape according to which the morphology of the GNFs depends. The BET surface area of these GNFs was $207\text{ m}^2/\text{g}$.

3.3 CNTs–polymer (polyacrylamide) composites

To study the surface morphologies of MWNTs–PAM composite films scanning electron microscopy studies were carried out. The SEM micrographs of MWNTs (~ 5 wt%)–PAM composite film using purified and ball-

Figure 3. TEM images of GNFs synthesized by Cu–Ni catalyst (a) reveals the planar form grown at 600°C; (b) reveals the helical form grown at 700°C.

Figure 4. SEM micrographs of (a) MWNTs (~5 wt%) (ball-milled)–PAM composite film, Inset: MWNTs (purified)–PAM composite film. (b) MWNTs (~40 wt%)–PAM composite film Inset is for functionalized MWNTs (~40 wt%)–PAM composite film.

milled MWNTs is shown in figure 4a. The purified MWNTs (without ball-milling treatment) were present mainly in the form of agglomerates (inset of figure 4a), whereas the ball-milled MWNTs were dispersed more uniformly, confirming much better dispersion of MWNTs in PAM matrix. Figure 4b shows SEM image of MWNTs (purified)–PAM composite with 40 wt% loading of nanotubes. The MWNTs were uniformly distributed throughout the polymer matrix.

To get a good dispersion for CNTs in matrix to receive a high interfacial bonding between CNTs and polymer matrix, it is necessary to attach some organic functional groups on the surface of CNTs. In the present investigation, amine group was attached onto the surface of MWNTs. Inset of figure 4b shows the SEM images of

MWNTs (~40 wt%)–PAM composite films with amine functionalized MWNTs. The length of MWNTs decreased due to acid treatments in functionalization process. The electrical transport property (d.c. electrical conductivity) of the MWNTs–PAM composite was measured using the four-probe technique. The room-temperature conductivity of the MWNTs–PAM composites at different loading of MWNTs is shown in figure 5. The d.c. electrical conductivity of pure PAM film was $\sim 1.05 \times 10^{-7}$ S/cm. No change in conductivity was observed at 5 and 10 wt% MWNTs (purified). The conductivity reaches $\sim 3.48 \times 10^{-6}$ S/cm at 15 wt% MWNTs loading, which is one order of magnitude higher than that of PAM. At 40 wt% MWNTs loading, the conductivity of MWNTs–PAM composite was ~ 1.2 S/cm. Thus the con-

ductivity of MWNTs (~40 wt%)-PAM composite increases by seven orders of magnitude.

The conductivity increase with MWNTs content fraction (wt%) indicates a typical percolation behavior. The MWNTs (ball-milled) (~5 wt%)-PAM composite film shows increase in conductivity by three orders of magnitude higher than pure PAM film. The significant increase in conductivity suggests that dispersion of nanotubes was increased due to ball-milling process. The electrical conductivity of functionalized MWNTs-PAM composite film was the same as that of pure PAM at 5 and 15 wt% MWNTs loadings. At 20 and 40 wt% functionalized MWNTs loading, the conductivity was three and four orders of magnitude higher than pure PAM film. The decrease in electrical conductivity of MWNTs

(functionalized)-PAM composite as compared to MWNTs (purified)-PAM was expected. The electrical conductivity decreased due to the presence of functional group on the surface of CNTs. Further investigations regarding mechanical properties of MWNTs-PAM composites are being carried out and results will be forthcoming.

3.4 Graphene

A definitive identification of graphene can be made by analysis of XRD pattern. The XRD pattern of graphite, graphite oxide and graphene are shown in figure 6. XRD pattern of graphite shows an intense peak $2\theta = 26.4^\circ$. This peak corresponds to 002 plane of graphite with interlayer spacing of 0.34 nm. In the XRD pattern of graphite oxide a new peak appears at $2\theta = 13.2^\circ$, corresponding to the 002 plane of graphite oxide (Schniepp *et al* 2003). The interlayer spacing of GO is ~0.75 nm, which is significantly larger than that of graphite, due to intercalating oxide functional groups. The mechanism of exfoliation is mainly the expansion of CO_2 evolved into the interstices between the graphene sheets during rapid heating. The disappearance of native graphite XRD peaks in the XRD pattern of as-prepared graphene sample supports the formation of graphene sheets. The SEM image of graphene sample is shown in figure 7a, where the sheets are highly agglomerated and particles have a fluffy morphology. The TEM image of graphene sample shows a wrinkled paper like structure in low magnification. The selected area diffraction (SAED) pattern of graphene sheets is shown in inset of figure 7b. The diffraction pattern indicates the formation of few layers of graphene.

We have measured the d.c. electrical conductivity of as-prepared graphene sample by four probe setup which was ~10.6 S/cm at room temperature. The characterization of graphene sample and investigation of graphene-polymer composites are being carried out and results will be forthcoming.

4. Conclusions

Based on the present investigations, the following conclusions can be drawn:

(I) Multi-walled CNTs were prepared in high yield by spray pyrolysis of castor oil-ferrocene solution at 850°C under Ar atmosphere. The C-N nanotubes were synthesized by modifying the castor oil-ferrocene precursor with ammonia at 850°C . The morphology of the as-grown CNTs and C-N nanotubes has been verified by SEM and TEM. The advantage of the present synthesis technique is the simplicity and use of low cost and easily available precursors.

Figure 5. Room temperature electrical conductivity of MWNTs-PAM composite film vs the MWNTs loading (wt%).

Figure 6. XRD patterns of graphite, graphite oxide and graphene samples.

Figure 7. SEM (a) and TEM (b) images of graphene samples. Inset of (b) shows the SAED pattern of graphene sample.

(II) Graphitic nanofibres (GNFs) were successfully synthesized by employing fine particles of Cu–Ni as a catalyst. Catalyst assisted thermal decomposition of hydrocarbon gas method was used for the synthesis of GNFs at two different temperatures, 600°C and 700°C, by using H₂ as carrier gas and C₂H₂ as a feedstock gas. Microstructural analysis shows that the planar GNFs are formed at 600°C and helical GNFs at 700°C. BET analysis shows that these GNFs possessed high surface area (207 m²/g).

(III) We have prepared MWNTs–PAM composite films using as-purified, ball-milled and functionalized MWNTs. The effect of ball-milling and functionalization of CNTs on the properties (dispersion, electrical conductivity) of composites have been studied. The present investigations revealed that in PAM film, conductivity at room temperature is 1.05×10^{-7} S/cm and for MWNT (~40 wt%)–PAM film, it increases to 1.2 S/cm i.e. by seven orders of magnitude. SEM micrographs show that nanotubes dispersion improved through ball-milling of MWNTs at low nanotubes loading (~5 wt%). Functionalization of nanotubes can improve the interfacial bonding between the nanotubes and polymer matrix. But electrical conductivity decreased due to attachment of functional group onto CNT surface.

(IV) We have successfully synthesized graphene sheets by thermal exfoliation of graphite oxide at 1050°C under Ar atmosphere. XRD pattern of as-prepared graphene sample did not present any diffraction peak indicating the formation of graphene. The TEM images reveal a wrinkled paper like structure.

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