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Effect of substrate and catalyst on formation of aligned Carbon nanotubes by CVD technique

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The extraordinary properties of carbon nanotubes (CNTs) their potential applications have lead to concerted efforts worldwide to produce these materials in more economical way. In our laboratory, we have launched programs to synthesize aligned carbon nanomaterials through chemical methods. Carbon nanotubes have been synthesized using Xylene as carbon precursor, silica, iron and nickel as catalyst in solid (as substrate) as well as in vapour forms (iron as catalyst). The effect of these catalysts on the growth, yield and alignment of carbon nanotubes has been studied. These have been found to be deposited preferentially on substrates kept in the reactor or on its walls depending on their relative activities. Well aligned carbon nanotubes are formed with iron in vapour forms in the mixture of carbon source and well dispersed nickel in amorphous silica as substrate. Randomly oriented nanotubes are formed on nickel as substrate. The yield under optimum iron/xylene mixture has been found to increase with quartz, nickel, silica and nickel in silica as substrates. These carbon nanomaterials have been characterized using XRD, TEM, SEM and thermal analysis techniques. Carbon nanotubes heat treated to higher temperatures have been found to be more thermally stable in oxidizing environment.

Key words: carbon nanotubes, CVD, deposition on substrates, purification, heat treatment

1. INTRODUCTION

Carbon has indeed played an important role in nanoscience world with the discovery of fullerenes followed by carbon nanotubes [1,2]. Carbon nanomaterials exist in various forms, as layered materials, nano clusters, fullerenes, nanofibers and nanotubes. Among these carbon nanotubes (CNTs) have been attracting much attention because of their unique physical properties and potential for large industrial applications. These materials find wider applications as sensors, energy storage, electrodes for lithium ion batteries as well as in microelectronic and communication devices. Interest is also growing for their application in structural fields. Moreover, industrial applications require large-scale production of carbon nanotubes in less expensive and easier way. Amongst various methods to synthesize CNTs, catalytic chemical vapour deposition method promises to be simple, more controllable and suitable for large-scale production. The properties of the end product depend on chirarity, diameter, linearity and purity, which are in turn controlled by the fabrication method. There is widespread interest in growing controllably aligned carbon nanotubes, and significant progress has been made in this direction in recent years. Many reports have appeared on growth of aligned arrays of nanotubes, by using preformed substrates [3-6]. However, the role of substrates is still not clear and hunt is on to find optimum substrate. The preparation of substrate either in monolith form (Silicon or Silica) or in embedded form needs special instrumentation and is often quite expensive. Solution route is the most versatile inexpensive method to synthesize multielement ceramics or metal embedded oxides ceramics. However, there is not much open literature on application of solution route to develop substrates of desired composition for growing carbon nanotubes. This paper reports on the experimental results obtained in our department on formation of carbon nanotubes on substrates containing varying amount of Si, O, Ni, Fe etc prepared through sol-gel route.

2. EXPERIMENTAL

2.1 The CVD apparatus

The schematic diagram of experimental set-up used for the preparation of carbon nanotubes by CVD method is shown in Figure 1. The reactor is made of 550 mm long quartz tube of 35 mm inner diameter placed in a tubular electrical furnace. The substrate, which is the site of the nanomaterials formation, was placed in pyrolysis zone of the horizontal quartz reactor. The temperature control in the pyrolysis zone was carried out using programmable temperature controller. The reactor is connected to gas delivery system wherein inert gas/hydrocarbon vapors can be introduced at controlled rate.

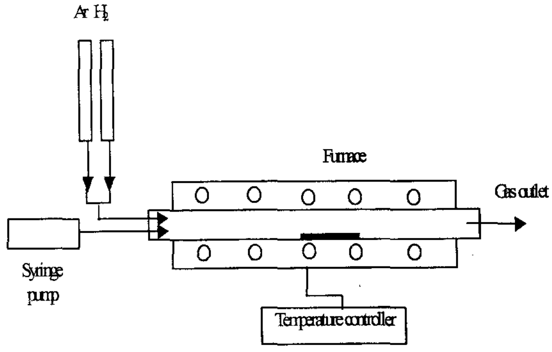

Fig.1. Schematic diagram of the setup for growth of CNTs

2.2 Materials used

Carbon source: Xylene Catalyst: Ferrocene

Substrates: Silica, Quartz, Nickel and Silica-Nickel (SNS) Nickel used was in the form of metallic sheet. Amorphous silica was prepared in plate form using sol-gel method from hydrolyzed TEOS containing 1:4:2 molar ratio of TEOS: Water: Ethanol. In order to have uniform distribution of nickel particles in silica substrate, these were prepared from nickel nitrate solution and hydrolysed TEOS using sol-gel method. These were reduced with flowing hydrogen at 550°C to ultimately give Silica-Nickel substrates.

2.4 Synthesis of carbon nanotubes

The hydrocarbon source (xylene) containing about 1-2 wt.% of catalyst (ferrocene) was injected in the reactor at 700°C-800°C with the help of syringe pump. In hydrocarbon solution, xylene is carbon source and ferrocene act as catalyst for the nanotube formation. The injection feed rate, reaction time and temperature were varied in series of experiments. After the reaction, the furnace was allowed to cool under argon atmosphere. All substrates, used in these studies, were weighed before and after the reaction to determine the amount of carbon produced at different sites within the reactor.

2.5 Purification of carbon nanotubes

For potential use of carbon nanotubes in electrical and thermal applications these must be devoid of impurities such as metals and silica. In present studies purification process was carried out by dissolving 300 mg of as-prepared carbon product in HCl (50%) for 24 hrs. The acid treated carbon product was then dissolved in 1:1 mixture of HF-HNO_3 for 20 hrs and washed with distilled water. The washed carbon nanotubes were heat treated to 1800°C for further removal of non-carbonaceous impurities remaining after acid treatment and alignment of graphene layers to remove defects.

2.6 Characterization of carbon nanotubes

The samples were viewed under Scanning Electron microscope (SEM) Hitachi S-3000N to ascertain formation of ultra thin elongated structures (fibers or tubes). Transmission electron microscope (TEM) Philips, Tecnai-20 was used to examine the tubular nature of the samples. XRD analysis of the nanomaterials was carried out by X-Ray Diffractometer Philips, X'pert model. TGA of carbon materials was carried out on Mettler Thermal Analysis system TA 4000 with TG50 for getting information about amount of catalyst present in the product and also to study oxidation behaviour of carbon nanotubes

3. RESULTS AND DISCUSSION

3.1 Effect of processing parameters on growth of carbon nanotubes

The CNTs arrays were grown on Silica, Quartz, Nickel and Silica-nickel substrates at 800°C for a total time of 30 mins, 60 mins and 120 mins with different ferrocene concentration in xylene and at varying feeding rates. Since the reactor is made up of quartz tube, its inner wall also acted as growth sites for CNTs. The nanotube arrays could be easily pealed off from the substrate surface without destroying the arrays integrity. The growth direction of carbon nanotubes was towards the axial center of the tube. The carbon nanotubes in the arrays are very clean with uniform diameter of about 25-65 nm. The Fig. 2 Shows dependence of carbon depositions on total quantity of solution and solution feed rate and time of deposition on nickel/silica substrate. As seen in fig. 2, for same feeding rate, i.e. 0.5 ml/min, CNTs deposition increases with feeding time, i.e. with total amount of solution. Further, the deposition is found to be higher for higher feed rate. 15 ml of solution injected at rate of 0.5 ml/min gave higher carbon yield than 20 ml of solution injected at rate of 0.3 ml/min. The higher feed rate of solution provides abundant Fe particles and carbon source. The continuous feeding method secures the continuous supply of Fe catalyst particles and carbon source during the continuous growth process of aligned carbon nanotubes. These trapped particles may maintain a rapid continuous growth of carbon nanotubes. So, higher feed rate gives better results and provides higher growth rate of carbon nanotubes. The feed rate not only enhances the growth density and yield but also size of the nanotubes. Similarly, the growth was more for samples prepared from 2% ferrocene in xylene than for those prepared from 1% ferocene solution in xylene. However, the impurity content in former samples was also higher. It was also observed that the carbon nanotubes deposition increased with increase of substrate area.

3.3 Role of catalyst/substrate in carbon nanotube growth

The vertically carbon nanotubes grown on silica, quartz and silica-nickel substrates were found to be aligned starting from the base and perpendicular to the base. In case of silica-nickel based substrate, nickel performs secondary role of catalyst for the formation of CNTs. Bimetallic complex of iron and nickel gave better results in terms of growth density and alignment as compared to quartz substrates (Fig.3). Aligned carbon nanotubes with high growth density and close contact were grown on nickel/silica substrates. As such, iron particles and nickel provide growth centers, Vander Walls interaction between the tubes keeps them growing in a well-aligned manner. As far as the role of nickel and iron as catalysts in growth and alignment of carbon nanotubes is concerned, it has been found that the latter has dominant role in growth and alignment of carbon nanotubes while the former though catalyzes the growth of carbon nanotubes, no indication has been found of their influence in aligning the carbon nanotubes. This was also reflected when nickel plate alone was kept in container and only Xylene was introduced in the reactor. There was scanty formation of carbon nanotubes, arranged in random manner. Similarly, the nanotube growth density on quartz substrates was found to be lower than on silica and nickel-silica substrate.

3.4 Impurities in carbon nanotubes

Carbon nanotubes grown through ferrocene-xylene solutions in presence of nickel are known to contain metallic impurities. The HF-HNO_3 along with strong HCl treatment facilitates removal of trapped metals and silica phase in the carbon nanotubes. Thermo gravimetric analysis of carbon nanotubes under oxygen containing environment was used to estimate the amount of impurities present in the tubes as such and after purification. Fig. 4 shows TGA graph of CNTs before and after purification. The impurity content is found to increase with increasing concentration of ferrocene from 1% to 2%. The impurity content increases from 8-10% for 1% Ferrocene-Xylene solution to 10-20% for CNTs grown from 2% ferrocene in xylene solution. Fig. 4b shows TGA curve of chemically treated (purified) carbon nanotubes. It shows that the impurity content decreases from 8-10% to 1-2%. It confirms that most of metal catalyst was leached out by acid purification. Further it is seen that both carbon nanotubes as such as well as purified nanotubes exhibit similar oxidation behaviour. The onset of oxidation of as-prepared and acid treated carbon nanotubes is found to be around 550°C. On the other hand the onset of oxidation of carbon nanotubes heat treated at 1800°C is found to be around 650°C (Fig.4c). This is attributable to the ordering of the graphene layers of the carbon nanotubes. Ordering gets enhanced by heat treatment of carbon nanotubes. The heat treatment of acid treated carbon nanotubes at 1800°C further removed the remaining impurities as shown by thermo gravimetric analysis of heat treated carbon nanotubes.

3.5 Scanning electron microscopy of carbon nanotubes

Fig. 5 shows SEM micrographs of the carbon nanotubes grown on different substrates. Figure 5 a shows the scanning electron micrographs of carbon nanotubes formed in random manner on nickel plate alone. CNT arrays grown on the surface of silica-nickel substrate (SNS) are shown in Fig.5b. This image presents features of CNTs with densely packed and vertically aligned growth mechanism on the surface of substrate. All of the tubes for a growth time of 60 minutes are almost of the same height around 650 μm, so the average growth rate calculated is about 10.8 μm/min. The length of the carbon nanotubes was found to be double about 1300μm as from 2% Ferrocene-Xylene solution as compared to that from 1% Ferrocene-Xylene solution. This suggests mutual effect of reaction time and concentration of Ferrocene. So, if the deposition time increases, the carbon nanotube length is found to be increasing on quartz as well as nickel-silica substrate. But overall growth rate is higher in case of nickel-silica substrate.

Fig. 6 shows TEM image of CNTs produced from ferrocene-xylene mixture on substrate surface. It reveals the flexibility present in carbon nanotubes.

3.6 X-ray diffraction studies of carbon nanotubes

X-ray diffractogram of the carbon nanotubes showed peaks at around 2θ= 21.78° and 37.78° in addition to the peak at 2θ=26° Former correspond to presence of silica and iron compounds respectively. The intensity of peak at 2θ=26° gets increased with chemical treatment and heat treatment of carbon nanotubes at 1800°C. Further XRD of heat treated samples suggested that carbon nanotubes heat treated to 1800°C exhibit well graphitic structure as compared to as-prepared and chemical treated carbon nanotubes.

4. CONCLUSIONS

The catalytic decomposition of Ferrocene-Xylene mixture over substrates leads to formation of carbon nanotubes. The injection CVD method provides the basis for synthesis of aligned CNTs with vertical and horizontal fashion growth on suitable substrate. Studies on different substrates revealed that carbon deposition depend on the substrate type. Metallic complex catalyst system shows enhanced growth of carbon nanotubes. The silica and silica-nickel substrate shows better results as compared to nickel and quartz substrate. The length and diameter of the carbon nanotubes were found to be dependant on reaction time and amount of catalyst present in the carbon precursor. This can be done by increasing active sites for the carbon deposition on the substrates. Additionally, the production of large volumes of aligned carbon nanotubes is of interest in composites applications because CVD method shows better results in terms of quantity of carbon nanotubes as well as amount of impurity is less. The CVD method is very simple and efficient method to develop carbon nanomaterials with desired configurations.

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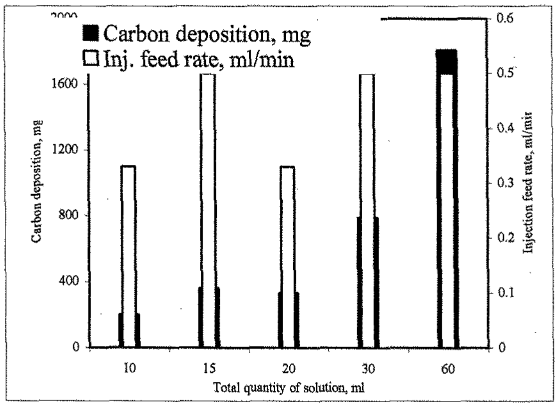


Figure 2. Relation between carbon deposition yield, injection feed rate of solution and total quantity of solution containing 2wt% ferrocene in Xylene

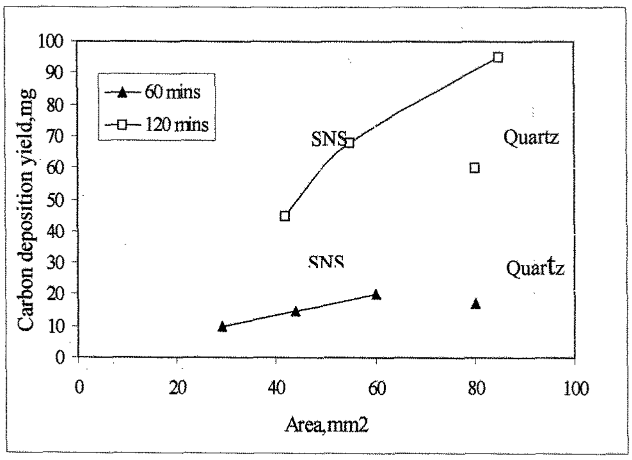


Figure 3. Deposition of carbon nanotubes from 2wt% ferrocene in xylene solution on SNS and Quartz surface at constant feeding rate.

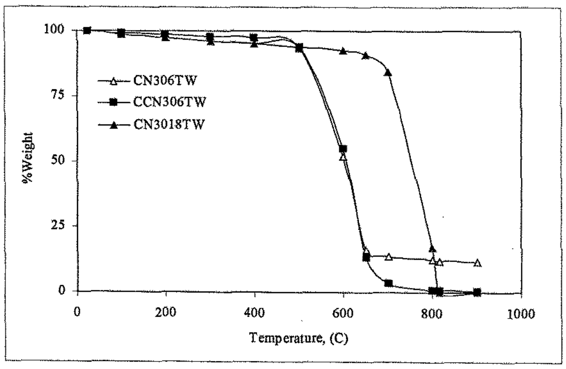
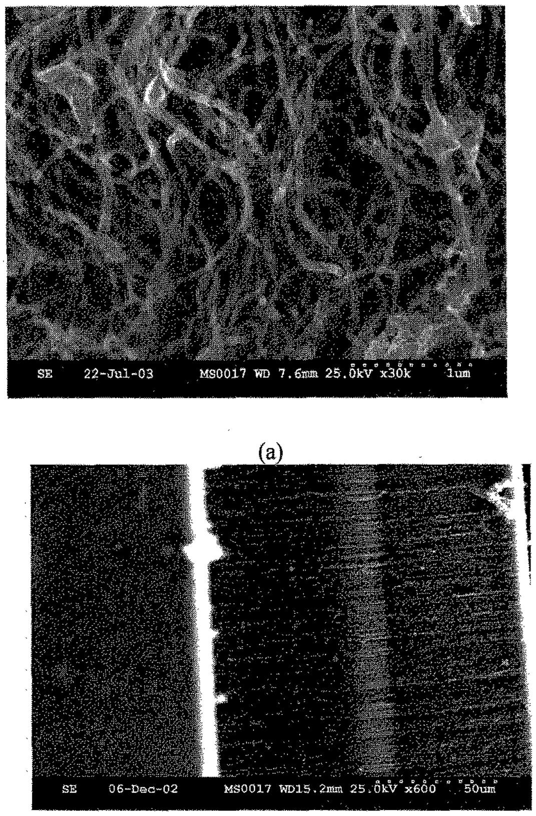


Figure 4. TGA of (a) as-prepared, (b) chemical treated and (c) heat treated CNTs



(a)

(b)

Figure 5. SEM micrographs of (a) randomly oriented carbon nanotubes growth on Nickel plate
(b) aligned CNTs on SNS surface

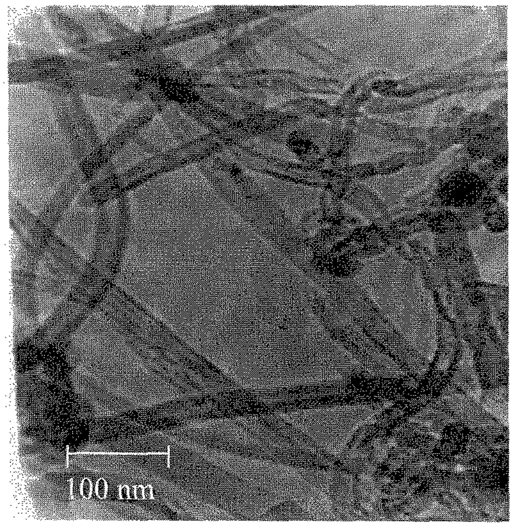


Figure 6. TEM image of CNTs produced from ferrocene-xylene mixture.

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