Studies of yield and nature of carbon nanostructures synthesized by pyrolysis of ferrocene and hydrogen adsorption studies of carbon nanotubes

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Abstract

The yield and nature of carbon nanostructures synthesized by the pyrolysis of acetylene using different quartz reactors and gas flow rates are investigated. The effect of these influential parameters on the growth of various carbon nanostructures has been studied and discussed. With a quartz reactor of inner diameter 24 mm and at gas flow rates of 40 and 600 sccm of acetylene and argon, respectively, good quality carbon nanotubes with better yield have been obtained. The samples were characterized by X-ray diffraction, BET surface area measurements, scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The hydrogenation behavior of these as-grown and purified carbon nanotubes was carried out at room temperature and in the pressure range 10–100 bar, using a high pressure Sieverts apparatus. The hydrogen storage capacity of carbon nanotubes was found to increase, after subjecting to acid treatment and heat treatment. The maximum hydrogen adsorption capacity of 2.1 wt% is obtained at 298 K and 100 bar for carbon nanotubes after acid treatment and air oxidation.

Keywords: Carbon nanotubes; Pyrolysis; Hydrogen storage

1. Introduction

The most important factor to be considered regarding hydrogen being used as an energy carrier in various applications is its safe and efficient storage. The current technologies for hydrogen storage are either unsafe or expensive as in the case of compressed gas storage or liquefaction respectively [1]. Metal hydrides are promising [2], however they have low storage capacities when compared to the standard set up by the US Department of energy (DOE) for hydrogen fuel based vehicles [3], and hence other advanced materials are being investigated for their hydrogen storage capacities.

Recent reports of high reversible adsorption of molecular hydrogen in carbon nanotubes (CNTs), alkali-doped graphite and graphitic nanofibers (GNFs) [4–7] have stimulated tremendous interests in the research community to exploit the lightweight novel carbon materials as ideal candidates for hydrogen storage devices. Due to the wetting properties of carbon nanotubes, their inner hollow cavity can serve as a storage medium for other materials. They are able to draw liquid or gas inside by capillarity [8]. This has initiated interest, both experimental and theoretical studies, in storage of hydrogen in single-walled nanotubes (SWNTs) [9–11]. In our recent work, the removal of catalytic impurities and amorphous carbon from the as-synthesized carbon nanotubes from pyrolysis of acetylene over alloy hydride catalysts has resulted in the increased hydrogen sorption capacity of 3.3 wt% at 298 K and 100 bar [12].

Since 1993, the catalytic growth of carbon nanotubes based on the decomposition of hydrocarbons has been widely studied [13,14]. Many parameters like the nature of catalyst, temperature, growth time, gas flow rates and quartz reactor dimensions affect the nature and yield of carbon
deposits in the case of carbon nanostructures synthesized using thermal CVD method [15]. Emmenegger et al. [16] have investigated the growth mechanism of CNTs grown over Fe catalyst on aluminum by chemical vapor deposition (CVD) and have shown that large CNT density can be obtained only by controlling precisely the parameters such as the time of deposition, the temperature and the catalyst concentration during the CVD process. We have investigated the deposition of carbon species by thermal CVD using the pyrolysis of acetylene with ferrocene as precursor. By keeping the growth temperature and the catalyst same, our aim is to study the effects of the influential parameters such as gas flow rates and the quartz reactor dimensions. In this paper, we present the results on the yield and the nature of carbon nanostructures obtained from the pyrolysis of acetylene, with different quartz tube dimensions and gas flow rates. Based on the yield and the nature of carbon deposits, the process has been optimized for the synthesis of carbon nanotubes. In addition, hydrogen adsorption studies on these as-synthesized and purified CNTs have been carried out and are discussed.

2. Experimental

2.1. Synthesis of carbon nanotubes

Carbon nanotubes were synthesized by the catalytic decomposition method [13]. In our experiment, acetylene is used as the carbon source, argon as the carrier gas and ferrocene as the precursor for catalytic nanoparticles of iron. The apparatus consisted of a two-stage furnace system fitted with a quartz tube. Carbon deposition was studied with different gas flow rates at 1050°C, using a quartz reactor of 24 mm inner diameter and 1000 mm length. We have also investigated the effect of quartz tube diameter on the yield and nature of carbon deposition, at constant gas flow rates of acetylene (40 sccm) and argon (600 sccm). The parameters have been optimized for a better yield of carbon nanotubes. Each time, 100 mg of ferrocene was taken in a quartz boat and placed inside the quartz reactor. The furnace with ferrocene was heated to 350°C, after the temperature of the second furnace reached 1050°C. Acetylene gas was allowed for 30 min. Argon flow was maintained through out the experiment till the furnace was cooled to 100°C. Carbon nanostructures were brought out from the reaction zone by argon and were deposited as a black film at the cooler end of the quartz tube. The as-synthesized samples were characterized by X-ray diffraction, BET surface area measurements, scanning electron microscopy (SEM; JEOL JSM 840 A), transmission electron microscopy (TEM; JEM-200 FX II) and FT—Raman spectroscopy (FRA 106 Bruker). The as-grown CNTs were refluxed with con HNO3 for 24 h, followed by washing with de-ionized water several times and then the sample was dried in air for 30 min at 100°C. This was followed by air oxidation at 350°C for 1 h to remove the amorphous carbon and to open the ends of CNTs [17].

2.2. Hydrogen adsorption measurements

The hydrogen adsorption studies of the as-synthesized and purified carbon nanotubes were carried out using a high-pressure Sieverts apparatus, in the pressure range 10−100 bar and at room temperature. Before exposing to hydrogen, the carbon nanotubes were activated by heating up to a temperature of 175°C under a vacuum of 10−6 Torr for 5 h. Hydrogen was allowed at 100°C and then cooled to room temperature. The equilibrium pressure was observed for about 12 h and was noted. As in a high-pressure experiment, the pressure changes arising from temperature variations can be mistakenly interpreted as substantial sorption, room temperature in our laboratory was maintained at 25 ± 1°C. The volume occupied by the sample was also taken into account, as the carbon samples are of low density. All these effects including the inherent leakage of the system were taken into account in the analysis of the hydrogen adsorption results [18]. The pressure–composition relationships were obtained by calculating the hydrogen storage capacity in wt% from the pressure drop during the hydrogen adsorption at constant temperature. After each cycle, the sample was degassed for 5 h at 175°C under a vacuum of 10−6 Torr.

3. Results and discussions

3.1. Morphological characterization of carbon nanostructures

Carbon deposition was studied with different flow rates of acetylene and argon using the same quartz tube reactor of 24 mm inner diameter (1000 mm length), at 1050°C. After the decomposition of acetylene, the weight of carbon deposit was calculated using the equation

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\text{Carbon deposit (\%)} = 100\left(\frac{m_{\text{tot}} - m_{\text{cat}}}{m_{\text{cat}}}\right)
\]

where \( m_{\text{cat}} \) is the initial amount of the catalyst (before reaction) and \( m_{\text{tot}} \) is the total weight of the sample after reaction. The gas flow rates were measured using the respective flow meters (Flometers; Instrumentation engineers, India), which were calibrated at 1 bar and 25°C. At flow rates of 30 and 600 sccm of acetylene and argon, respectively, nanobeads of carbon were obtained as shown in Fig. 1a. Good quality carbon nanotubes together with traces of catalyst particles and amorphous carbon were obtained as seen in Fig. 1b. With higher acetylene feed (50 sccm), keeping the argon flow at 600 sccm, few nanotubes were obtained along with more of carbon coated particles as seen in Fig. 1c. Thick fibers of carbon along with catalyst particles and amorphous carbon were obtained (Fig. 1d), with flow rates of 60 sccm (acetylene) and 600 sccm (argon). With acetylene flow rate of 40 sccm and the argon flow rate increased to 700 sccm, nanobeads of carbon with few
thick fibers were seen (Fig. 2a). At higher acetylene flow rates, the rate of nanotube growth was lower than that of pyrolytic decomposition, which would have resulted in the formation of amorphous carbon. Also at lower flow rates of argon, the residence time of acetylene in the reaction zone would be more, which would further result in the deposition of amorphous carbon. The higher argon flow rate would have swept the catalyst particles away from the reaction zone, resulting in the formation of carbon nano beads. Moreover, the residence time of acetylene in the reaction zone, an important factor for the growth of carbon nanotubes, might have considerably reduced with a higher flow rate of argon. The weight of the carbon deposit passed through a maximum as a function of the gas flow rate. This could be due to the short residence time of acetylene gas at the catalyst active sites for higher gas flow rates. The yield of carbon nanostructures (Table 1) is found to have been affected by the deactivation of the catalyst particles, due to the formation of the carbon coated particles, which further decreases the pyrolysis of acetylene, as the catalyst also promotes the pyrolysis of acetylene apart from serving as nucleation sites. Thus the flow rate of acetylene and argon plays an important role in the formation of different carbon nanostructures. Good quality carbon nanotubes were obtained using a quartz reactor of inner diameter 24 mm (1000 mm length) and gas flow rates of 40 sccm (acetylene) and 600 sccm (argon). We have also carried out the experiment by varying the inner diameter of the quartz tube, keeping the acetylene and argon flow rates constant (40 and 600 sccm of acetylene and argon, respectively). The optimum experimental conditions for the production of the carbon nanotubes were established from the SEM measurements according to the amount of nanotubes observed and the quality of these tubes. Table 2 summarizes the results and observations on the yield and nature of carbon deposits on different quartz tube diameters. Well dispersed thick fibers were obtained with a quartz reactor of 29 mm inner diameter at a reaction temperature of 1050°C (Fig. 2b). Few nanotubes with amorphous carbon and more of catalyst particles were seen in the carbon soot deposited at 1050°C with a quartz reactor of 20 mm inner diameter (Fig. 2c). Carbon deposits were not obtained with a quartz reactor of inner diameter 10 mm, under our experimental conditions. The amount and the nature of the deposited carbon were found to depend strongly on the quartz tube diameter at constant gas flow rates. As the length of the quartz tube is kept constant through out the experiment, with smaller tube diameter, the local pressure created in the reaction zone will be higher and as a result the mean free path of the gas molecules will be more. This would further result in the increased velocity of gas molecules flowing through the tube. Hence, the variation of quartz tube dimension (inner diameter) also influence the nature and yield of carbon nanostructures deposited, as the actual gas flow rates in the reaction zone is varied in this process. Thus we have established the optimum combination of the gas flow
rates and the quartz reactor, to produce good quality carbon nanotubes. Quartz reactor of inner diameter 24 mm with acetylene and argon flow rates at 40 and 600 sccm, respectively, were used for the synthesis of CNTs, as the yield and nature of carbon deposition were found to be good and reproducible (Table 1).

In order to remove the amorphous carbon and the catalyst particles, the as-grown CNTs were refluxed with con HNO₃ for 24 h followed by washing with de-ionized water several times and then the sample was dried in air for 30 min at 100°C. This was followed by air oxidation at 350°C for 1 h. The yield of carbon nanostructures was calculated from the weight of the carbon deposit (%), before purification process.

3.2. Structural and microstructural characterization of carbon nanotubes

Specific surface area was measured for the as-synthesized samples (by Quantachrome, NOVA 1000), which was calculated to be 11.1 m²/g. Size distribution of the pores as shown in Fig. 3 reveals that this sample has a higher volume percentage of pores with size of 7.5 nm. Fig. 4 shows the X-ray diffraction of the as-synthesized CNTs. The (0 0 2) and (1 0 1) peaks of graphitic carbon are seen, the other peaks corresponding to that of catalytic impurities. A TEM image of CNTs with few catalytic particles inside is shown.
Fig. 3. Pore width distribution of as-synthesized carbon nanotubes prepared with quartz tube of inner diameter 24 mm.

Fig. 4. Powder X-ray diffractogram of as-grown carbon nanotubes.

Fig. 5. TEM image of carbon nanotubes with some catalyst particles.

in Fig. 5. The carbon nanotubes were featured by an outer diameter of 20–40 nm and with a hollow core of approximately 5–10 nm. Fig. 6 shows the Raman spectra of the as-prepared carbon nanotubes excited by a 1064 nm laser. The spectrum consists of mainly two peaks at 1296 and 1589 cm\(^{-1}\), which are designated as the tangential modes of carbon nanotubes [19]. The peak at 1589 cm\(^{-1}\) is due to the Raman-active \(E_{2g}\) mode analogous to that of graphite [20]. A slight red shift was observed for the \(D\)-band of our sample, which was located at 1296 cm\(^{-1}\), as the \(D\)-band frequency shows a strong linear dependence on the excitation laser energy (\(E_{\text{laser}}\)), which is further attributed to the electronic transition between bands, which is in resonance with the incident photon [21]. This is mainly derived from the disordered carbon and defects of MWNTs, which is a feature common to all \(sp^2\) hybridized disordered carbon materials. The suggested growth mechanism could be the dissociation of acetylene on the Fe nanoparticles carried over to the reaction zone by argon, and the dissolution and diffusion of carbon through these metal particles, and finally ends up with the precipitation of carbon at the rear faces of the Fe particle to form CNTs [22]. But interestingly, the TEM image in Fig. 5 shows catalyst particles inside the tubes and also at the tips. This further shows a similarity with the vapor–liquid–solid (VLS) mechanism, as the catalyst particle seen inside and at the tip of the tube could be the solidified form of the liquid-phase metal particle [23].

3.3. Hydrogen adsorption characteristics of carbon nanotubes

Hydrogen adsorption measurements were carried out in the pressure range 10–100 bar and at room temperature, using a high-pressure Sieverts apparatus. The system was calibrated at various initial pressures and the sample cell volume has been measured with van der Waals correction for the volume of the gas molecules and molecular interactions. Several blank tests were carried out at different initial pressures and the drop in pressure during the same time interval as that of the experiment was taken in to account while calculating the sample cell volume and hence for the precise measurement of the hydrogen adsorption capacity [18]. Each
time, over 300 mg of CNTs were used. The sample was evacuated to $10^{-6}$ Torr and activated by heating to 175°C for 5 h, after flushing with H$_2$ for 2–3 times. The temperature was reduced to 100°C and H$_2$ was allowed to interact with the sample subsequently and then directly cooled to room temperature. The equilibrium pressure drop was observed for about 12 h and was noted. Fig. 7 shows the hydrogen adsorption isotherms of carbon nanotubes. The amount of hydrogen adsorbed by the sample was calculated from the drop in pressure. The carbon nanotubes obtained after the acid treatment and heat treatment was also loaded and hydrogen adsorption studies were carried out. The as-grown nanotubes generally have closed ends. The hydrogen molecules could be physically adsorbed on the external nanotube walls [24]. However, sample which was subjected to treatment such as oxidation and acid washing, which could open their ends effectively, showed increased hydrogen sorption capacity, as hydrogen could have entered nanotubes through their ends. In the present work, a maximum storage capacity of 2.1 wt% was obtained at room temperature and at 100 bar for purified and heat treated CNTs, while a storage capacity of 1.7 wt% was observed for as-synthesized CNTs at the same experimental conditions (Fig. 7). The removal of catalytic impurities and amorphous carbon, with effective treatment with conc HNO$_3$ and further heat treatment would have added to the enhanced hydrogen sorption capacity. Zuttel et al. [25] have presented a model in which the surface adsorption of a monolayer of hydrogen leads to a maximum storage capacity of 3.3 wt%. The recent reports of 2.9 wt% of adsorption of hydrogen in carbon nanotubes at room temperature, measured by tangent-mass method [26] confirm the reproducibility of the hydrogen adsorption in carbon nanotubes. In our as-grown samples, the maximum storage capacity of 1.7 wt% could be due to the monolayer of hydrogen molecules adsorbed at the surface of the carbon nanotubes. A maximum storage capacity of 2.1 wt% points out that the ends of the tubes would not have fully opened after the acid treatment and air oxidation, limiting the availability of inner sites for hydrogen molecules to condense. Hence, it may be possible to further improve the hydrogen adsorption capacity with effective purification and heat treatment and further work is in progress.

4. Conclusions

From the growth of CNTs by pyrolysis technique, it has been shown that the gas flow rates and the quartz reactor dimensions are influential parameters for the growth of various carbon nanostructures using thermal CVD. The diameter of the quartz reactor and the gas flow rates are optimized for better yield and quality of the carbon nanotubes, prepared by the pyrolysis of acetylene. With a quartz reactor of inner diameter 24 mm, good quality carbon nanotubes with better yield are obtained with gas flow rates of 40 and 600 sccm of acetylene and argon, respectively. The hydrogen storage capacity in these carbon nanotubes is found to be increased after subjecting them to heat treatment and acid treatment and a maximum hydrogen storage capacity of 2.1 wt% at 298 K and at 100 bar is obtained.

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References

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