Investigation of Synthetic Strategies of Carbon Spheres by Chemical Vapour Deposition Method

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Abstract

The carbon microspheres (CMSs) have been synthesised by chemical vapour deposition (CVD) technique in the presence of catalyst through the pyrolysis of acetylene in a single electrically heated horizontal furnace. Systematic studies show that the size, distribution and the order of graphitisation of CMSs have been varied by different catalyst/support system. The resulting CMSs have been characterized by Scanning Electron Microscope and Raman Spectroscopy. Results show that Fe/Mo/AIP and Fe/Co/AIP catalyst/support produced CMSs at 900^oC and below this temperature carbon nanotubes have been synthesised. The diameter range of CMSs is 300 to 600 nm. The catalyst ferrocene/xylene mixture synthesised CMSs within the temperature range of 700 to 900^oC and the diameter of these CMSs varies from 500-2000 nm. Poly acronitrile (PAN) film doped with iron as catalyst also produced carbon microspheres distributed over the preheated surface of PAN film at 700^oC. The diameter of these CMSs is 600 to 750 nm. Raman studies show that the I_G/I_D values for the synthesized samples are 1.03, 1.21, 1.67 and 1.79. The lower value of I_G/I_D for the carbon spheres for Fe/Mo/AIP and Fe/Co/AIP system indicates the lower the degree of graphitisation. The higher the value of I_G/I_D for sample synthesized by using ferrocene/xylene mixture and on PAN film has higher I_G/I_D value1.67 and 1.79 respectively indicating the higher the degree of graphitization.

Key words Chemical Vapor Deposition, Carbon Microsphere, Catalyst, Raman Spectroscopy, Electron Microscopy

Introduction

Carbon materials have attracted the attention of human beings from prehistoric time. Recent developments in the synthesis of carbonaceous materials have lead to the synthesis of several new forms of carbon such as carbon nanotubes (CNTs) [1], carbon nanofibres (CNFs) [2], carbon onions [3], cone shaped graphitic particles [4], carbon micro trees [5], carbon spheres [6] and carbon microcoils [7] etc. Out of these carbon spheres are attracted many researchers due to a number of applications,

which include lithium ion batteries [8], catalyst support material [9] and high-strength material [10]. These CMSs have been prepared by chemical vapour deposition (CVD) method, arc discharge, laser ablation, autoclave process etc. All these methods are also used for the synthesis of CNTs or CNFs [11-16]. Wang et al [12] synthesize carbon spheres by a mixed-valent oxide-catalytic carbonization (MVOCC) process in which methane was decomposed at 1100^oC with the diameter 210 nm by CVD process. In most of the report the process of the synthesis of carbon sphere via CVD process involved the double heating system, one is for the vaporization of precursor materials and another for the cracking and redeposition of the carbon material. Sharon et al produced CMSs [13] with the diameter in the range of 250-850 nm by catalytic process from camphor vapour at 1000 ^{o}C using ferrocene as catalyst precursor in a double heated system. Some studies have also been reported the synthesis of carbon microspheres in the absence of catalyst by the direct pyrolysis of benzene, hexane, cyclohexane and ethane. Yamada et al [14] have also reported the production CMSs from the pitch. However among the different methods of the synthesis CVD is one of the most promising methods for large-scale production of CMSs. In addition to the high yield, it can produce CMSs supported any substrate for its application purposes. Large scale and controlled growth of CMSs is required for catalytic and adsorption application and for electrochemical studies a film of CMSs is required. In CVD technique there are number of parameters which control the shape, size and the graphitization of CMSs such as precursor material (catalyst, support, carbon source etc.), reaction temperature, flow of feedstock gas, flow of inert gas, preheating of the catalyst support system etc. Recently a significant research has been performed for the synthesis of CMSs by CVD process improving the experimental conditions [17, 18]. In this paper we investigate the various experimental conditions of CVD for the synthesis of CMSs supported over a substrate in film form or as amorphous powder for their different applications. According to serial experiments this paper explores the different possibility of the synthesis of CMSs in a single step.

Experimental

All the chemicals were purchased from sigma-aldrich and used as such without further purification. The samples were prepared by chemical vapor deposition method in a single horizontal furnace using different precursor materials. Details of the instrument used are given elsewhere [19]. Summary of the precursors materials are given in table 1.

Table 1: Experimental conditions

Sr. No.	Carbon source	Substrate	Catalyst	Reaction Temperature
1	Acetylene	AIP	Fe/Mo	900^{o}C
2	Acetylene	AIP	Fe/Co	900^{o}C
3	o-Xylene mixture	NIL	Fe	700 ^{o}C - 900 ^{o}C
4	Acetylene	PAN	Fe	700^{o}C

Synthesis of CMSs in presence of Fe/Mo/AIP & Fe/Co/AIP catalyst support system

In the first and second reaction conditions, carbon microspheres are prepared by the pyrolysis of acetylene over bimetallic catalyst containing Fe/Mo and Fe/Co transition metals supported over the hydrolyzed Aluminium Isopropoxide (AIP) under the inert atmosphere of nitrogen at 900^{o}C reaction temperature. Details of the catalyst preparation and experimental conditions have been discussed elsewhere [19].

Synthesis of CMSs in presence of ferrocene/xylene mixture

In the third reaction process 1.5% ferrocene/o-xylene mixture is used as a feed stock for the synthesis of carbon microspheres. For this an alumina boat containing the ferrocene/o-xylene mixture is put at the inlet end of the furnace. The temperature of the furnace varied from 650°C to 950°C. During the reaction, the flow of nitrogen is maintained at 500ml/min. The reaction time is 30 minutes. After complete CVD reaction process dull black cotton like material is deposited on quartz plate placed at in the midpoint of furnace. After natural cooling under nitrogen atmosphere the product is collected from the furnace.

Synthesis of CMSs in presence of Fe embedded in PAN film

In the fourth reaction process a film of Poly Acro Nitrile (PAN) containing 10% Iron acetyl acetonate 98% (Aldrich) is used as substrate material for the growth of product. In previous methods of synthesis product is obtained as black powder, while in this process product is grown on a film, which can be directly used for its application. Before the reaction PAN film is preheated up to 1100°C under nitrogen and hydrogen atmosphere. The flow of these gases is maintained in 1:1 ratio. After reaching the furnace temperature 1100°C, furnace is allowed for natural cooling up to 700°C in nitrogen atmosphere. At this temperature cracking of acetylene is carried out for 30 minutes. At this reaction temperature the flow of nitrogen, hydrogen and acetylene is maintained at 200ml/min, 100ml/min and 100ml/min respectively. After 30 minutes CVD process furnace is allowed for natural cooling under nitrogen atmosphere. The resultant film is collected for further characterization.

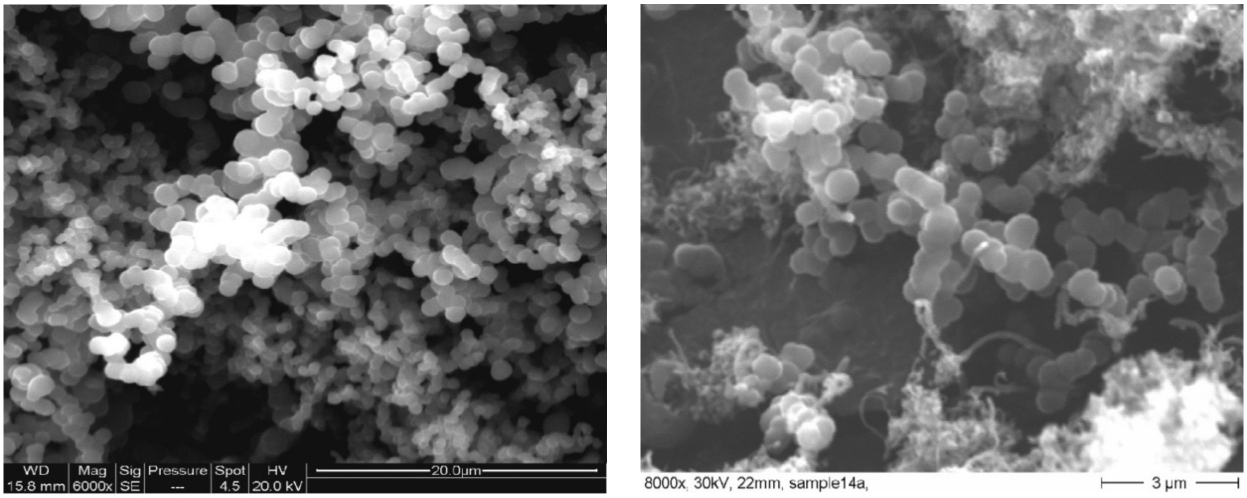
Characterisation

The samples have been characterized by SEM (JEOL JSM 840) to study the morphology, diameter and uniformity of the samples. For SEM observations the samples are dispersed on double adhesive carbon tap mounted on SEM stuff. Raman Spectroscopy (Renishaw Raman) is performed at 514.5 nm wavelength produced from Ar ion Laser.

Results and Discussion

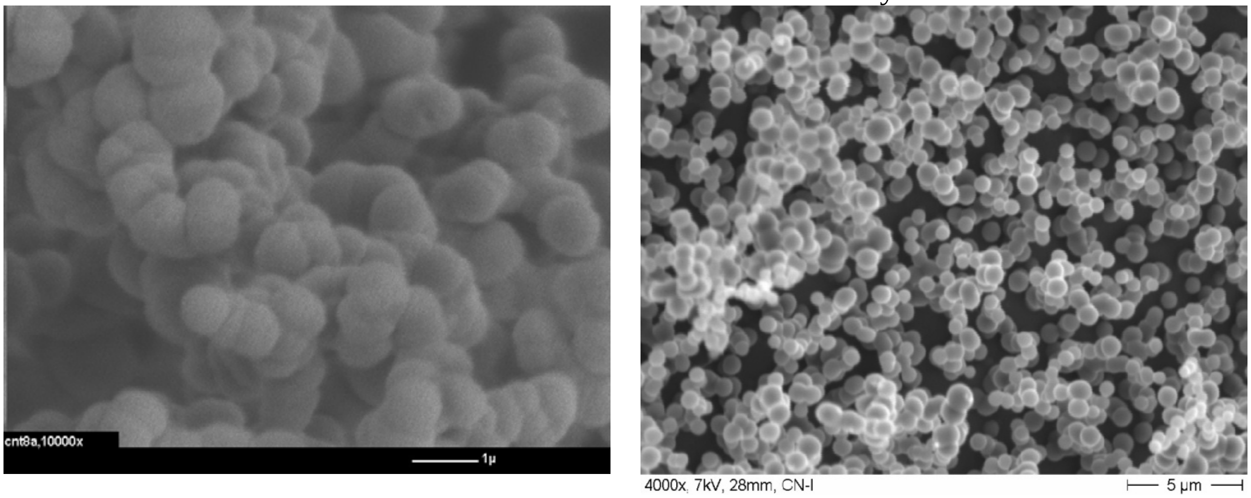
The synthesis of CMSs was achieved by catalytic chemical vapour deposition process using different catalyst/support systems and acetylene as the carbon precursor. The mechanism of the formation of carbon spheres consists of the dissociation of acetylene in to C and H. After that carbon starts to polymerize forming basic structural units (BSUs). The final deposition of these units depends on the precursor, heating treatment, feeding time and the interface between the carbon atoms and their surroundings during thermal process. The catalyst act as a template providing nucleation site for the subsequent formation of spheres [18].

The SEM images of the samples prepared at 900°C by using the catalysts Fe/Mo/AIP & Fe/Co/AIP show spherical granules of carbon having the diameter in the range of 300-600 nm (Fig.1a & 1b). Microscopic studies show that for the catalyst Fe/Co/AIP along with spheres, fibrous growth also takes place, while in case of Fe/Mo/AIP carbon spheres are obtained. It has been already discussed [19] that for these catalyst systems with the reaction temperature the morphology of the resultant products is also changed. For these catalysts at 700°C to 800°C reaction temperature only CNTs are produced, while at 900°C spheres of carbon are observed. Such observation confirmed that any catalyst/support systems, which are responsible for the growth of CNTs, can also be used for the preparation of carbon spheres. SEM images of the product obtained by CVD of the ferrocene/Xylene mixture at the reaction temperature 700°C - 900°C shows the presence of carbon spheres (Fig. 1c). When the reaction is carried out at 600°C, no deposition takes place.



(a) Carbon beads synthesized by using the catalyst Fe/Mo/AIP

(b) Carbon beads synthesized by using the catalyst Fe/Co/AIP



(c) Carbon beads synthesized by the pyrolysis of ferrocene/xylene mixture

(d) Carbon beads synthesized over the PAN film

Figure 1 SEM images of carbon beads

The SEM images show that the samples are not uniform with respect to diameter. The diameter of these carbon spheres varies from 500-2000 nm. Sample prepared at 700°C has the carbon spheres having the diameter 550-2000 nm. But most of the spheres are in the range of 850-1100 nm. At 850°C diameter distribution of the carbon spheres is in the range of 850-1400 nm (most of the spheres: 1100 nm) and 950°C the spheres are of 500-1700 nm (most of the spheres: 1400 nm). SEM image reveals that the carbon spheres grown on the PAN film are 500nm - 1µ. More than 75% carbon spheres are 600-750 nm. All these carbon spheres are dispersed on PAN film (Fig.1d). Results show that the CMSs synthesized under the experimental condition 1 and 3 have narrow diameter distribution while the CMSs synthesized under the experimental condition 2 have broad range of diameter. Substrates play an important role to control the size of catalyst particle, which further control the size of products. Each catalyst support / system has catalyst embedded in the pores of substrate and during reaction procedure at the optimum temperature these pores released the catalyst particles of specific size which accelerate the synthesis of CMSs under the given experimental conditions. Since in the experimental condition 1, 2 and 4 the catalysts are supported over the substrate, the substrates control the size catalyst particles in two ways (i) size of pore (ii) adsorption force in between the catalyst particles and substrate reduce the chances of aggregation resulting in the formation of smaller size catalyst nanoparticles and CMSs also. While under the experimental condition 3 catalyst is free from substrate and the nuclei synthesised during heating further go to the process of agglomrisation due to the lack of adsorption force between catalyst particles and the substrate, which results the larger size catalyst particle and the larger CMSs. In addition to size control substrate oriented synthesis of CMSs can directly be used for application purposes.

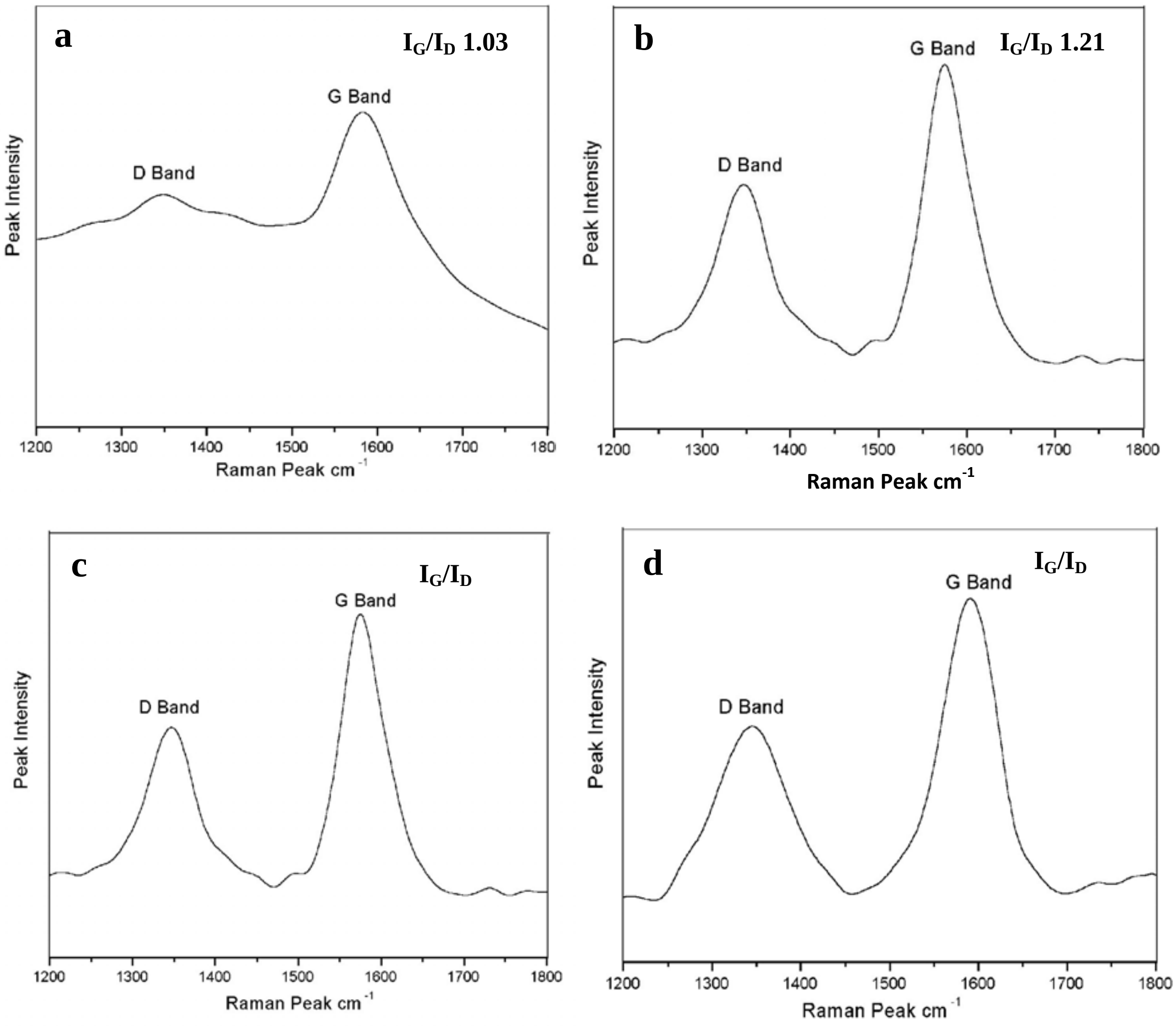


Figure. 2. Raman spectra of samples (a) Raman spectrum of carbon beads synthesized by using the catalyst Fe/Mo/AIP (b) Raman spectrum of carbon beads synthesized by using the catalyst Fe/Co/AIP (c) Raman spectrum of carbon beads synthesized by the pyrolysis of ferrocene/xylene mixture (d) Raman spectrum of carbon beads synthesized over the PAN film

The Raman Spectra of all these samples showed two peaks at around 1335 cm^{-1} and 1595 cm^{--1}, which are correspond to the typical Raman peaks of graphitized carbon spheres. The peak at 1335 cm^{-1} (D band) could be assigned to the vibrations of carbon atoms with dangling bonds in planner terminations of disordered graphite. The peak at 1595 cm^{-1} (G band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2 bonded carbon atoms [20]. The intensity ratio of these G and D bands I_G/I_D reflecting the degree of graphitization of carbon spheres and the presence of amount of disorder carbon. Higher value of I_G/I_D indicates the higher the degree of graphitization. In this report the I_G/I_D values for the synthesized samples are 1.03, 1.21, 1.67 and 1.79 (Fig: 2). The lower value of I_G/I_D for the carbon spheres for Fe/Mo/AIP and Fe/Co/AIP system indicates the lower the degree of graphitisation. The higher the value of I_G/I_D for sample synthesized by using ferrocene/xylene mixture and on PAN film have higher I_G/I_D value1.67 and 1.79 respectively indicating the higher the degree of graphitization.

Raman studies show, that the experimental conditions plays a significant role on the graphitization of CMSs. Inorganic additives accelerate [21] the graphitization of carbon with lower temperature, which is called catalytic graphitization. In previous works numerous transition metals have been used as precursor for the graphitization. Out of different transition metals iron has been reported to have good catalytic property to convert carbon into graphitic material at lower temperature. Results show that degree of graphitization increases with the concentration of iron content in carbon feed stock. The graphitization of CMSs is also affected with the reaction temperature. CMSs synthesised at 900^oC (in reaction 1 & 2) has lower graphitization as compared to the CMSs synthesised in remaining two conditions. Finally the results show that how the experimental conditions and catalyst govern the size and order of graphitization of the synthesised product.

Conclusions

We have demonstrated the pyrolysis of acetylene in presence of Fe/Mo/AIP and Fe/Co/AIP catalyst/support system. Results show that these catalysts are active for the synthesis of CMSs at 900^oC. Below this temperature they are active for the synthesis of CNTs only. Further the cracking ferrocene/xylene mixture produces CMSs within the temperature of 700^oC to 900^oC, below 700^oC only amorphous carbon is deposited. CMSs distributed over PAN film are suitable for application purposes due to its direct use in devices having the layer of CMSs. The comparative studies of the synthesised CMSs by Raman Spectroscopy shows that the CMSs synthesized by using ferrocene/xylene mixture and on PAN film have higher the degree of graphitization as compared to Fe/Mo/AIP and Fe/Co/AIP catalyst support system. The experiments conducted with different catalyst support system indicates that the morphology and size distribution of CMSs can be controlled by varying the pyrolytic conditions (catalyst and temperature) and the production of CMSs can be scaled up based on our application purposes as for as a filler or as a conductive film.

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