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Large-scale synthesis of segmented carbon nanofibers by catalytic decomposition of acetylene on fan shaped foam Ni

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Large-scale synthesis of segmented carbon nanofibers (SCNFs) by catalytic decomposition of acetylene on fan shaped foam Ni in an improved conventional reactor is reported. The procedure can be scaled up for semi-continuous production of the deposits. The effects of the reaction conditions on the growth of the segmented carbon nanofibers are discussed. Samples of the deposits in as-prepared state were examined by means of XRD, SEM, TEM and HRTEM. The results indicate that a semi-continuous synthesis of 10 g of deposits with about 90% segmented nanofibers was obtained at flow rate of acetylene 15 ml/min and hydrogen 150 ml/min at temperature 600°C for 30 min. The HRTEM image revealed that the fibers are stacked with well ordered graphitic platelets intermittently spaced by less ordered graphitic platelets perpendicular to the axis of the fiber. The growth mechanism of the segmented carbon nanofibers is also discussed.

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1. Introduction

Carbon fibers (also known as carbon filaments) can be grown from the catalytic decomposition of certain hydrocarbons over small metal particles such as iron, cobalt, nickel, and some of their alloys [1–4]. Carbon nanofibers that appeared in a number of different forms, such as cylindrical hollow cored, straight, branched, helical and coiled structures [5–8] have also been synthesized for almost decade. The newly discovered properties and potential applications of the products have made them one of the novel materials [9]. In recent years, intense research activities have been highlighted on large-scale synthesis and mass production of the products. Kim and co-workers [10] used supported catalyst powders to produce carbon nanofibers. They reported that 25 g of highly graphitic carbon nanofibers could be generated from the interaction of 100 mg of a powdered catalyst with flowing ethylene at 600°C over a period of 4 h. Rodriguez *et al.* [11] indicated that the structure and the properties of the fibers could be tailored by careful control of a number of parameters including the nature of the surface, the composition of the gas-phase reactant, the temperature and the incorporation of either gas-phase or solid additives. Especially, the arrangement of the graphite platelets can be engineered to the desired geometries by choice of the correct catalyst system. Fan and co-workers [12] prepared pure vapor-grown carbon nanofibers (VGCNFs) with controllable diameters of 10–200 nm by an improved floating catalyst method, in which benzene was used for the carbon source and ferrocene for the catalyst precursor and reaction temperature was maintained at 1150–1200°C. It is concluded that the diameter of the fibers could be controlled by vaporizing temperature

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of ferrocene and the flow rate of benzene. Although the above conventional catalytic decomposition method using supported or unsupported transition metal powders as the catalysts is suitable for the production of large quantities of carbon nanofibers, the preparation of the supported catalysts is a tedious process and time-consuming job and the decomposition temperature of the floating catalyst precursor is very high. Soneda *et al.* reported that they used a stainless steel plate as catalyst and produced carbon filaments by the decomposition of CO recently, but their reaction lasted 100 h [13]. Therefore seeking for alternative forms of catalysts for easier preparation of the carbon nanofibers seems to have great significance for various industrial applications of carbon nanofibers.

In this work, an effective catalyst of commercially available foam Ni for large-scale synthesis and mass production of segmented carbon nanofibers by catalytic decomposition of acetylene is introduced. The effects of the reaction conditions on the growth of the segmented carbon nanofibers are reported. The structure and probably growth mechanism of the segmented carbon nanofibers are investigated.

2. Experimental

In order to synthesize a special structure of segmented carbon nanofibers, a thin slice catalyst must be prepared [11]. In this experiment we used commercially available high-porosity foam Ni as catalyst instead of conventional powdered or film catalysts. Firstly, it does not need special surface treatment, and therefore is simple and economical. Secondly, the porous structure of the foam nickel makes it easier to be fragmentized to thin slice catalyst at relatively low reaction temperature, so the whole synthesis system could be maintained at relatively low temperature. Thirdly, since the use of the catalyst foam nickel makes the manipulation of the system and the experimental process easier to be realized for the continuous or semi-continuous production. An improved conventional reactor system consisting of a long horizontal quartz tube (75 cm × 5 m) located in the chamber of a cylindrical electric furnace, with a catalyst conveyer and a product collector at its two ends. A disk-shaped foam Ni about 1.2 mm in thickness and 45 mm in diameter (grade 110, PPISM 70, from Shenzheng Energy Storage Corporation Limited, P.R. China) was first cut into sectors remaining the center portion of the disk uncut and then the sectors were twisted as fan blades. Afterwards, the fan shaped foam Ni was inserted vertically in the center of a cylindrical molybdenum boat, then pushed them into the quartz tube near the end of the furnace with a flow rate of N_2 (150 ml/min) for several minutes to drive oxygen out of the quartz tube and finally pushed them into the middle of the quartz tube with a flow rate of acetylene (99%) and hydrogen (99.99%) separately. The surfaces of the "fan blades" were towards the incoming reactant gases, the purpose for doing so is to make the catalyst Ni get sufficient contact with the reactant gases. After the scheduled reaction time, the acetylene and hydrogen flows were cut off, a nitrogen flow was introduced into the quartz tube and then the molybdenum boat was pulled to the end of the furnace waiting for cooling and sample collection, in the meanwhile, another fan shaped foam Ni catalyst was pushed into the molybdenum boat and the next run could be continued. Since the reaction temperature could be maintained constant, therefore, we could realize semi-continuous production of the products.

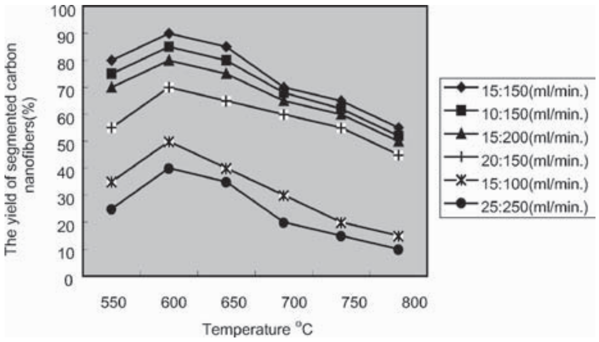

Figure 1 Effect of the reaction temperature on the growth of the segmented carbon nanofibers at different flow rate of acetylene and hydrogen (reaction time 30 min).

The flow rate of acetylene (10–25 ml/min) and the flow rate of hydrogen (100–250 ml/min) were measured with mass flow gauges (±0.1 ml/min.). The reactions were controlled at different temperatures ranging from 500°C to 800°C and allowed to last for 15–150 min. The effects of the above parameters on the growth of the segmented carbon nanofibers were examined, details of the experiment results are summarized in Fig. 1. The samples were observed using a Jeol2010 high resolution microscope with a point to point resolution of 0.19 nm, the X-ray diffraction (XRD) measurement were performed in a Philips diffractometer PW1710 with Cu K_α (0.15418 nm).

3. Results and discussion

3.1. Optimization of the growth conditions

Besides segmented carbon nanofibers the deposits also contains other forms of carbon nanofibers, amorphous carbon as well as a little remaining catalyst. In order to get high purity of the segmented carbon nanofibers, the effect of the reaction conditions on the growth of the segmented carbon nanofibers were investigated. The purity of the segmented carbon nanofibers in as prepared state was estimated by TEM observation. Fig. 1 shows the results of the effect of the reaction temperature on the growth of the segmented carbon nanofibers at different flow rate of acetylene and hydrogen. It was found that the optimized reaction temperature was 600°C. The quantity of deposits decreased at lower reaction temperature than 600°C, when the reaction temperature was less than 500°C, no segmented carbon nanofiber is formed. At higher temperature, the quantity of amorphous carbon deposits increased thus the purity of the segmented carbon nanofibers decreased. When the reaction temperature was over 800°C, the segmented carbon nanofibers decreased to below 10% even at the optimized flow rate of acetylene and hydrogen. The optimized flow rate of acetylene and hydrogen was found to be 15 and 150 ml/min respectively, when the temperature is at 600°, the segmented nanofibers attain to a maximum of 90% (Fig. 1). Lowering the flow rate of acetylene or raising that of hydrogen decreases the quantity of the segmented carbon nanofibers, but doesn't affect the purity of the product. On the other hand, raising the flow rate of acetylene or lowering that of hydrogen, or raising both rate of the acetylene and hydrogen, increases other forms of carbon nanofibers but decreases the segmented carbon nanofibers. In the meanwhile, the purity of the product is also affected.

The appropriate duration of the reaction was found to be 30–60 min under the above optimized reaction conditions. Shortening the growth process decreases the deposits thus decreases the amount of the segmented carbon nanofibers. Allowing longer reaction time than 60 min increases amorphous carbon around the segmented carbon nanofibers, thereby affects the purity of the product. In our experiment upon the end of each run, the cylindrical molybdenum boat was fully blocked with 10 g of the deposits with about 90% segmented carbon nanofibers under the optimized reaction conditions of the flow rate of acetylene 15 ml/min and hydrogen 150 ml/min, the reaction temperature 600°C and the reaction time 30 min.

3.2. Microstructure

Fig. 2 shows the typical SEM image of the deposits produced by the catalyst decomposition of acetylene on foam Ni at 600° for 30 min with the flow rate of acetylene 15 ml/min and hydrogen 150 ml/min. It clearly indicated that the deposits are almost pure carbon nanofibers with diameter ranged from tens to two hundred nanometers and few amorphous carbon and remaining catalyst present (Fig. 2). The high purity of the deposits indicates that the high-porosity foam Ni was extremely active at the reaction temperature, and it was an effective catalyst for the growth of carbon nanofibers, and the variation in diameter of the fibers indicates the variation in grain size of the active Ni catalyst. Therefore, it is supposed that the surface of the foam Ni underwent a fragmentation process producing tremendous amount of small-sized catalyst prior to the conformation of the carbon nanofibers. Since the primary porosity of the foam Ni is uneven so the size of the slice catalyst produced in the surface fragmentation process of the foam Ni is quite different, these may be responsible for the large variation in diameter of the carbon nanofibers.

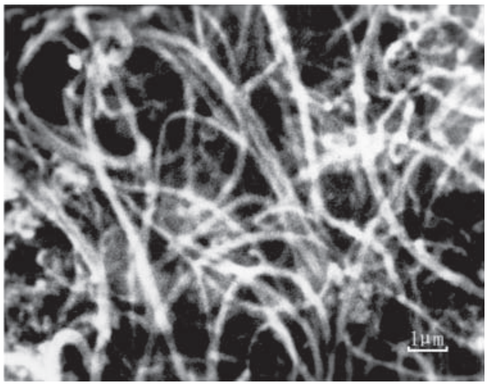

Figure 2 SEM image of the deposits prepared at the optimized conditions (Reaction temperature 600°C; Reaction time 30 min; Gas flow rate: C_2H_2 15 ml/min; and H_2 150 ml/min).

Figure 3 TEM image of the segmented carbon nanofibers (Reaction temperature 600°C; Reaction time 30 min.; Gas flow rate: C_2H_2 15 ml/min; and H_2 150 ml/min).

Fig. 3 shows the typical TEM image of the carbon nanofibers at the optimized reaction conditions. It is clearly shows a special morphology of the fibers that is quite different from the other forms of the coexisting carbon nanofibers [5–8]. The fibers are composed of a series of short segments that contains two kinds of sub-regions (black region and light region), and thereby we named it "segmented carbon nanofibers". This segmented structure can be seen more clearly in larger diameter nanofibers than the small ones. This means that the bigger sized catalytic particles were responsible for the formation of the segmented carbon nanofibers. X-ray diffraction analysis result shows that though the graphite (002), (100), (101) and (004) diffraction peaks are occurred but (002) and (004) diffraction peaks are apparently widened (Fig. 4). These indicate that the segmented carbon nanofibers were composed of a lot of graphitic crystallites. Fig. 5 shows the HRTEM image of the segmented carbon nanofiber. It is obvious from the image that the fiber was stacked with well ordered graphitic platelets (black region) that are intermittently spaced by less ordered graphitic platelets (light region) perpendicular to the axis of the fiber. Moreover, it can be also found that the crystallinitic graphite platelets were separated by a distance about several to over ten nanometers and in the crystallinitic graphite platelet an array of slit-shaped pores separated by a distance of 0.342 nm between two crystallinitic graphite platelets (Fig. 5), which is bigger than that of the ideal graphite lattice parameters (0.335 nm). This unique structure of the segmented carbon nanofiber, which consists of crystallinitic graphite platelets with larger graphite lattice parameters having virtually only edges exposed, provides this material with unique properties that are highly desirable for gas sorption applications.

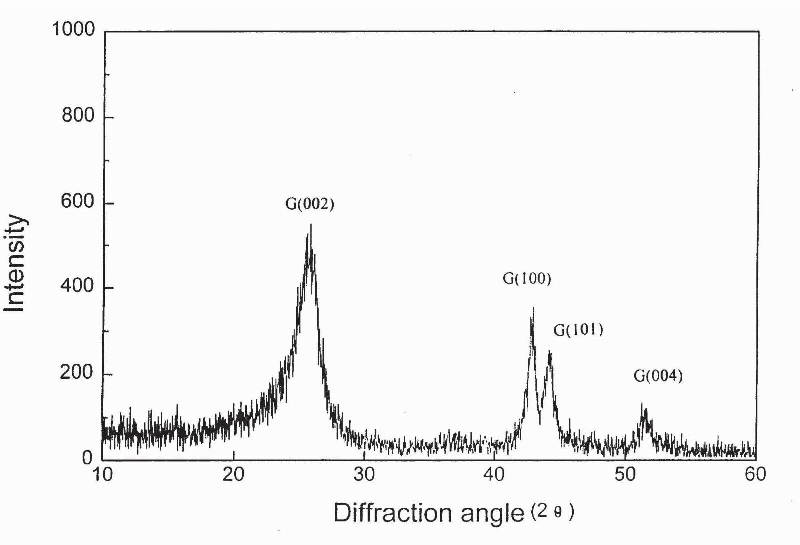

Figure 4 X-ray diffraction pattern of the segmented graphite nanofibers (Reaction temperature 600°C; Reaction time 30 min; Gas flow rate: C_2H_2 15 ml/min; and H_2 150 ml/min).

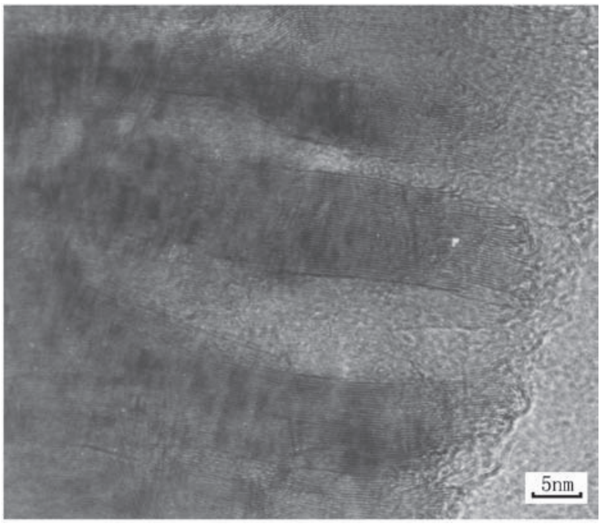

Figure 5 HRTEM image of the segmented carbon nanofiber showing the well ordered graphitic platelets intermittently spaced by less ordered graphitic platelets perpendicular to the fiber axis.

3.3. Growth mechanism

It is well known from surface science studies that the interaction of a giving gas molecule with a metal surface is frequently limited to curtain crystal faces of the solid [14], such as Ni, in (002) face it is capable of chemical dissociating the carbon-containing gases and adsorption of carbon atoms but unable to precipitate dissolved carbon atoms, while in (111), (311) and (220) faces they exhibit the reverse properties [15]. So when catalyst Ni adopt a thin slice shape, the small vertical faces of the catalyst Ni would be capable of dissociating hydrocarbon and the two large transverse faces would be more suitable for carbon precipitation to generate a structure in which the graphitic platelets are aligned parallel to the large faces and perpendicular to the fiber-axis [16]. In order to obtain this type of thin slice catalyst, we used foam Ni as catalyst since it could be fragmentized to thin slice shape with a relative lower reaction temperature. Lower reaction temperature was adopted because the catalyst particles tended to form a round shape at high temperature over 600°C [16], which is not suitable for the growth of the segmented nanofibers resulting in decrease of the quantity of the segmented carbon nanofibers. Since the diffusion of carbon through the metal catalyst is the rate-determining step [17] in the filament growth process, for the slice shaped catalyst, the diffusion path of the central region is long and the carbon concentration is relatively low. So carbon precipitates at the edge of the large transverse faces of the slice catalyst first and then the central region later. Once carbon precipitation occurs in the central region for a while, it becomes unsaturated because the carbon source is controlled by the diffusion process and the precipitation process is endothermic [18]. It needs time for carbon concentration to return to its original concentration and temperature. Obviously, such a carbon precipitation process in the central region is discontinuous. As a result, the carbon hexagonal platelets are formed only periodically parallel to the large transverse faces of the slice catalyst. When the carbon source is sufficient enough to continuously precipitate carbon in the central region, graphitic filaments would be formed while no segmented carbon nanofibers would be obtained. Therefore, in order to get high purity of the segmented carbon nanofibers, an appropriate flow rate of acetylene and reaction temperature must be carefully controlled.

4. Conclusion

A large scale synthesis of 10 g of deposits with about 90% segmented carbon nanofibers(SCNFs) in each run has been produced at the optimized reaction conditions by catalytic decomposition of acetylene on fan shaped foam Ni in an improved conventional small experimental reactor. The optimized reaction conditions were found to be the flow rate of acetylene 15 ml/min and hydrogen 150 ml/min, the reaction temperature 600°C and the reaction time 30 min. It has been proved that commercially available foam nickel is one kind of effective and simple catalyst precursor for high quality growth of segmented carbon nanofibers. Mass production of the segmented carbon nanofibers could therefore be expected after enlarging the small experimental reactor. The microstructure of the product shows that the fibers are stacked with well ordered graphitic platelets intermittently spaced by less ordered graphitic platelets perpendicular to the axis of the fiber, this unique structure of this material may be found application in gas sorption.

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