CONTROLLABLE SYNTHESIS OF CARBON ROPES SUPPORTED ON CAREON FOAM

Nan Xiao, Liman Fan, Zheng Ling, Ying Zhou, Zongbin Zhao, Jieshan Qiu

Carbon Research Laboratory, State Key Lab of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, Liaoning, China.

Introduction

The discovery of fullerenes in 1985 [1] opened avalanche of novel nanosized and microsized carbon materials with unique structures (e.g., carbon nanotubes [2], carbon onions [3], cone-shaped graphitic structures [4] and carbon micro-trees [5]). The assembly of functional nano-sized carbon materials into well-defined structures of controlled shape, location, orientation and density is required for many potential applications, such as field emitters, composites, hemical sensors and functional nanodevices [6, 7]. Under this driving force, both *in situ* growth and post-synthesis approaches have been explored for making ordered carbon nanofibers (CNF) architectures. In the present paper, the synthesis of microsized carbon ropes (CRs), which is tightly packed by CNFs with an orientation roughly parallel to the longitudinal axis of the CR, supported on the CF which was synthesized using polyurethane (PU) foam as template is discussed.

Experimental

In a typical run, commercial ester-type PU foams were immersed into a solution of PAA/N,N-dimethylacetamide (10 wt.%) and $Ni(NO_3)_2 \cdot 6H_2O$ with a PAA/Ni mass ratio of 100:4 that was made under stirring at room temperature (RT) for 3 h to make PAA/PU-Ni foams. The PAA/PU-Ni foams were dried at 60 °C for 10 h before use. The PAA/PU-Ni was heated to 700-900 °C at a heating rate of 2 °C/min and maintained at that temperature for 1 h in flowing nirtogen before being cooled down back to RT, yielding a black product denoted as Ni/CFx hereafter (x is 700, 800 and 900 referring to the heat treatment temperature.).

With the carbonized Ni/CFx as substrate, the CRs/CF composites were prepared in a horizontal quartz tube reactor by pyrolysis of C_2H_4 (50 mL/min) in mixture of flows of H_2, N_2 and SO_2 ($H_2/N_2/SO_2$ volume ratio of 70:29:1, total flow of 100 mL/min) for 30 min at 800 ^oC. Before introducing C_2H_4 into the reaction system, the CF substrate was firstly reduced at 600 ^oC in flowing H_2 for 30 min. The as-obtained samples were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and field emission scanning electron microscopy (FESEM).

Results and Discussion

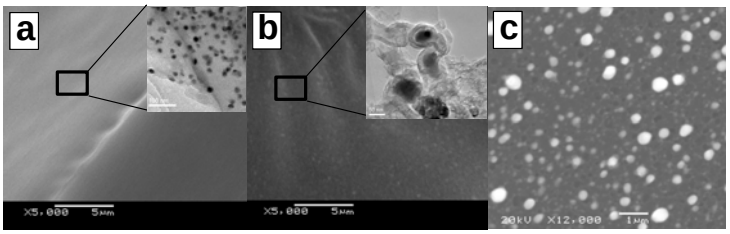

Fig. 1 SEM images of Ni/CFs obtained by carbonizing at (a) 700 ^oC, (b) 800 ^oC, and (c) 900^oC in flowing N_2.

One of the key concerns in describing the growth of CRs is the characteristics of their catalysts. TEM images show that the size of Ni particles increases as the heat treatment temperature increase from 700 to 800 ^oC (insets in Fig. 1a and b). In the case of 700 ^oC, Ni particles with a diameter of about 20 nm are homogeneously dispersed in carbon matrix (inset in Fig. 1a), while in the case of 800 ^oC, the Ni particle size is about 30-80 nm (inset in Fig. 1b) with graphitic shell could be observed. Microsized Ni particles on the surface of CF are formed abruptly at 900 ^oC, as shown in Fig. 1c.

After CCVD, only few CNFs can be found on the surface of the Ni/CF700 and Ni/CF800 (not shown here). While, the Ni/CF900 has compactly brushy microsized materials blanketing its surface, as shown in Fig. 2a. Fig. 2b shows that spheric Ni particle could be observed on the tip of every single carbon fiber. The further information available from FESEM images demonstrate that the micronsized fiber-like carbon material is a CR. Fig. 2c shows that the CR is tightly packed by CNFs with an orientation roughly parallel to the longitudinal axis of the rope. At the end of the CR, some loose CNFs protruding out randomly, as shown in Fig. 2d.

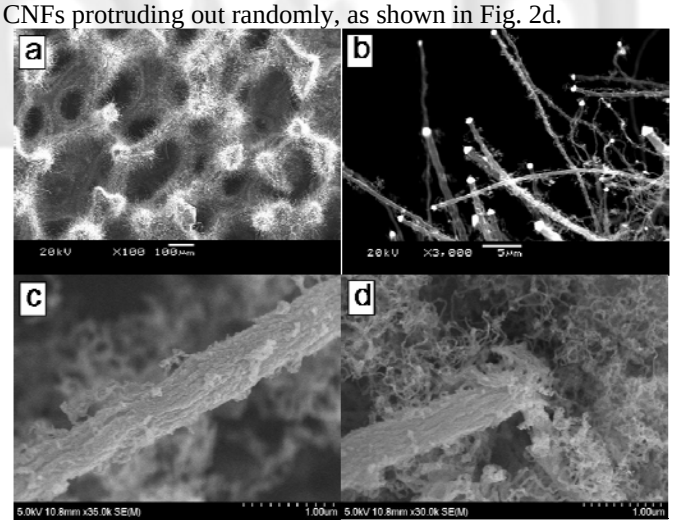

Fig. 2 SEM images of CRs/CFs

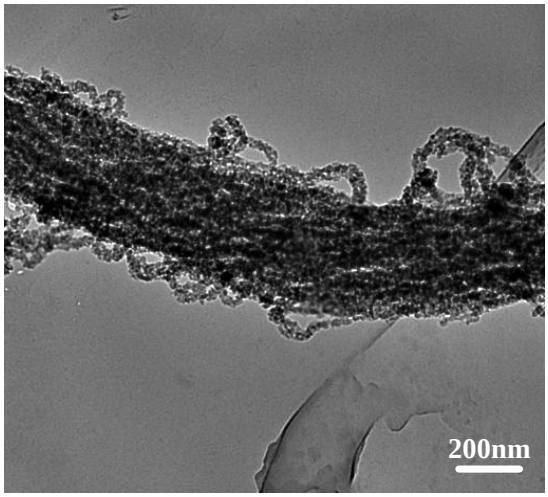

Fig. 3 TEM image of CR

TEM image (Fig. 3a) reveals that the CR, of which the diameter is about 500 nm, consists of a number of CNFs with an orientation roughly parallel to the longitudinal axis of the CR.

The effect of sulfur species in the CCVD on the production of CNFs has been explored [8, 9]. It is proposed that low levels of sulfur species could significantly increase the yield of carbon filaments by blocking part of the reaction sites available for the formation of graphitic layers, resulting in a longer catalyst lifetime. However, sharp drop in yield is observed for treatments with higher amounts of S species [10]. The same trend is observed in our experiment on the Ni/CFs obtained by carbonization at 700 and 800 ^{o}C in flowing N_2 (not shown here). This sharp drop in yield of CNFs indicates that sulfur is an efficient inhibitor in the growth of CNFs on the Ni/CF obtained by carbonization in flowing N_2. However, when the Ni/CFs are obtained by carbonization at 900 ^{o}C, the high level of sulfur does not lower the yield of carbon nanomaterials (Fig. 2a).

The detailed formation scheme of the CRs is not quite clear yet. We propose the following possible model to explain how these CRs are formed: at initial stage of carbonization, nanosized nickel oxide particles are formed and then reduced to nickel particles at low temperature (350 ^{o}C [11]). The as-formed nickel nanoparticles then merge to form larger particles. Meanwhile, Ni particles react with amorphous carbon contacted resulting in a graphite shells on the surface which will prevent the further coalescence of Ni particles below 800 ^{o}C(inset in Fig. 1b). When the temperature reaches 900 ^{o}C, large spheric Ni particles on the surface of CF are formed abruptly. During the CCVD process, CNFs grow from some faces of a single large Ni particle in an octopus-like mechanism [12] because the others have been blocked by the sulfur. With further synthesis, the octopus-like CNFs become denser and joint with each other resulting in CRs, which seems to involve the formation of S-rich carbon clusters.

The effects of the sulfur are currently under investigation with the aim of elucidating the growth mechanism of CRs. Undoubtedly, the growth of the CRs is a complex multicomponent reaction process. More detailed work is needed to clarify the formation mechanism of these CRs.

Conclusions

In conclusion, CRs/CF has been successfully fabricated with the addition of SO_2 by pyrolyzing C_2H_4 on the wall of Ni/CF900. The present technique will provide fresh impetus to the fundamental study on the growth of CRs. Further work is now in progress to evaluate the growth mechanism of CRs.

Acknowledgment. This work was partly supported by the NSFC (Nos. 20725619, 20836002, 50772017, 50972022).

References

[1] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C60: Buckminsterfullerene. Nature 1985;318:162-166.

[2] Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354:56-58.

[3] Ugarte D. Curling and closure of graphitic networks under electron-beam irradiation. Nature 1992;359:707-709.

[4] Krishnan A, Dujardin E, Treacy MMJ, Hugdahl J, Lynum S, Ebbesen TW. Graphitic cones and the nucleation of curved carbon surfaces. Nature 1997;388:451-454.

[5] Ajayan PM, Nugent JM, Siegel RW, Wei B, Kohler-Redlich Ph. Growth of carbon micro-trees. Nature 2000;404:243-243.

[6]Dai HJ.Carbon nanotubes: synthesis, integration, and properties. Acc Chem Res 2002; 35: 1035-1044.

[7]Fan SS, Chapline MG, Franklin NR, Tombler TW, Cassell AM, Dai HJ. Self-oriented regular arrays of carbon nanotubes and their field emission properties. Science1999;283:512-514.

[8] Fan, YY, Cheng HM, Wei YL, Su G, Shen ZH. Tailoring the diameters of vapor-grown carbon nanofibers. Carbon, 2000, 38(6):921-927.

[9] Kim M, N.Rodriguez, and R.Bak er, The Interplay Between Sulfur Adsorption and Carbon Deposition on Cobalt Catalysts. J. Catal. 1993 143, 449-463.

[10] Motta MS., Moisala A, Kinloch IA, Windle AH. The role of sulphur in the synthesis of carbon nanotubes by chemical vapour deposition at high temperatures. J. Nanoscience Nanotech. 2008, 8(5):2442-2449.

[11] Anton R. *In situ* TEM investigations of reactions of Ni, Fe and Fe-Ni alloy particles and their oxides with amorphous carbon. Carbon 2009; 47 (3): 856-865.

[12] Louis B, Vieira R, Carvalho A, Amadou J, Ledoux MJ, Pham-Huu C. Carbon nanofibers grown over graphite supported Ni catalyst: relationship between octopus-like growth mechanism and macro-shaping. Top. Catal., 2007, 45(1-4):75-80.