



Catalyst-free, low-temperature growth of high-surface area carbon nanoflakes on carbon cloth

Tsung-Chi Hung^{a,*}, Chia-Fu Chen^{b,**}, Chien-Chung Chen^c, Wha-Tzong Whang^a

^a Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta Hsieh Road, Hsinchu 30050, Taiwan

^b Department of Materials Science and Engineering, Ming Dao University, 369 Wen-Hua Road, Peetow, Chang Hua 52345, Taiwan

^c Energy and Resources Laboratory, Industrial Technology Research Institute, Hsinchu, Taiwan

ARTICLE INFO

Article history:

Received 10 September 2008

Accepted 6 October 2008

Available online 15 October 2008

Keywords:

Nanostructures

Chemical vapor deposition

Electrodes

ABSTRACT

We have used a microwave plasma-enhanced chemical vapor deposition system to synthesize two-dimensional (2D) and three-dimensional (3D) structures of carbon nanoflakes (CNFs). This catalyst-free, low-temperature synthesis involved introducing CO₂ and CH₄ as reactants at a specified ratio of 2:3. We obtained uniform 2D arrays of CNFs at lower microwave powers (200 or 300 W) and substrate temperatures (up to 420 °C); their thickness was close to 1 μm. At a microwave power of 400 W, we obtained a 3D architecture comprising the smallest nanoflakes reported to date. The specific surface area of the 3D structure was double that of the corresponding 2D arrays. We suspect that such structured carbon materials might have great potential for energy storage applications.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of C₆₀ in 1985 [1], nanometer-sized carbon materials have attracted much attention because of their large specific surface-to-volume ratio, high electrical conductivity [2–4], and their potential use in such applications as energy storage, electronic, and display devices [5–8]. Several other nanostructures have been developed, including carbon nanotubes (CNTs) and carbon nanoflakes (CNFs) [9,10]. Among these structures, we are interested in developing CNFs that possess graphitic structures, sharp edges, and large specific surface-to-volume ratios [11]. CNFs featuring very sharp and thin edges can be employed as field emission materials in backlit liquid crystal displays. Previous syntheses of CNFs have always required a catalyst and relatively high temperatures to provide two-dimensional (2D) networks perpendicular to the substrate on account of the self-potential near the electrode surface.

From an investigation of complex-plane impedance plots, Keiser et al. reported [12] that a 2D porous CNF structure is more suitable for electrochemical applications than are cylindrical or other porous structures. For use in other applications, however, the finite available surface area of a 2D film has some drawbacks. We believe that if CNF structures were not limited to 2D

architectures, then they might be suitable for use in energy storage systems, which require very large available surface area. In this paper, we report a relatively simple, catalyst-free, low-temperature microwave plasma-enhanced chemical vapor deposition (MPECVD) process – employing CO₂ and CH₄ as reactants – for the fabrication of 2D and three-dimensional (3D) CNFs on carbon cloth. The 2D arrays of CNFs arose as expected, whereas we obtained the 3D architectures when we applied a higher microwave power.

2. Experimental details

Carbon cloth (E-tech.) having an area of 1 cm × 1 cm served as the substrate for the growth of CNFs during MPECVD. The substrate was first activated with hydrogen plasma at a H₂ flow rate of 40 sccm at 300 W and 10 Torr for 10 min; a CO₂/CH₄ plasma was then applied at a power of 200, 300, or 400 W. The CO₂-to-CH₄ flow ratio was maintained at 2:3 and the growth process was performed at 10 Torr for 30 min. For comparison, other samples were subjected to the same deposition process, but without hydrogen plasma pretreatment. The color of the material deposited at 400 W was black; the other two products were gray. The substrate temperature was measured using an IR thermometer (Minolta TR-630) and a thermocouple in direct contact with the substrate holder. A JEOL JSM 6700 scanning electron microscope (SEM), a JEOL JEM 4000 high-resolution transmission electron microscope (HRTEM), and a micro-Raman scattering system (Jobin Yvon Lab-RAM HR; He–Ne laser; wavelength: 632.8 nm) were used to examine the structure of the product carbon materials. BET

* Corresponding author. Tel.: +886 3 5712121x55346; fax: +886 3 5724727.

** Corresponding author. Tel.: +886 4 8876660/1030; fax: +886 3 5724727.

E-mail addresses: volleyhung@yahoo.com.tw (T.-C. Hung), cfchen@mdu.edu.tw (C.-F. Chen).

measurements were performed for sample in a liquid nitrogen bath at 77 K using a Micromeritics TriStar 3000 instrument.

3. Results and discussion

Fig. 1 displays SEM images of the CNFs synthesized on the carbon cloth under various microwave powers after hydrogen plasma pretreatment. Fig. 1(a)–(c) presents images of the CNFs formed at 200 W and a relatively low substrate temperature (ca. 380 °C) for 5, 10, and 15 min, respectively. After 5 min, many tiny carbon islands were distributed uniformly on the substrate; on average, these islands were ca. 100 nm long and ca. 5 nm wide. After 10 min, the substrate was covered with structural carbon materials that evolved from the tiny islands; the CNFs were interlaced to form a carbon nest-like film. After 15 min, the CNFs all had a similar length of several micrometers and a height of ca.

1 μm . Even when operated for a longer length of time, the thickness of the film remained at 1 μm on account of lateral growth [13]. When we operated the system at 300 W for 15 min at substrate temperatures of up to 420 °C (Fig. 1(d)), the morphology of the product was similar to that obtained at 200 W, except that it contained more stretching branches attached to the surface of the major nanoflakes, such that a fraction of smaller pores existed. This phenomenon might have arisen from the presence of activated sites during the etching process in the CO_2/CH_4 plasma system. Oxygen-containing species (e.g., OH) play an important role in removing amorphous carbon and, thus, facilitate the formation of graphite structures [14]. The etching process might also have resulted in significant damage to the CNFs' surfaces to create dangling bonds of free carbon atoms as active sites for nucleation. We conclude that applying more power induces more tiny pores to form, i.e., a much smaller porous structure results. We obtained a

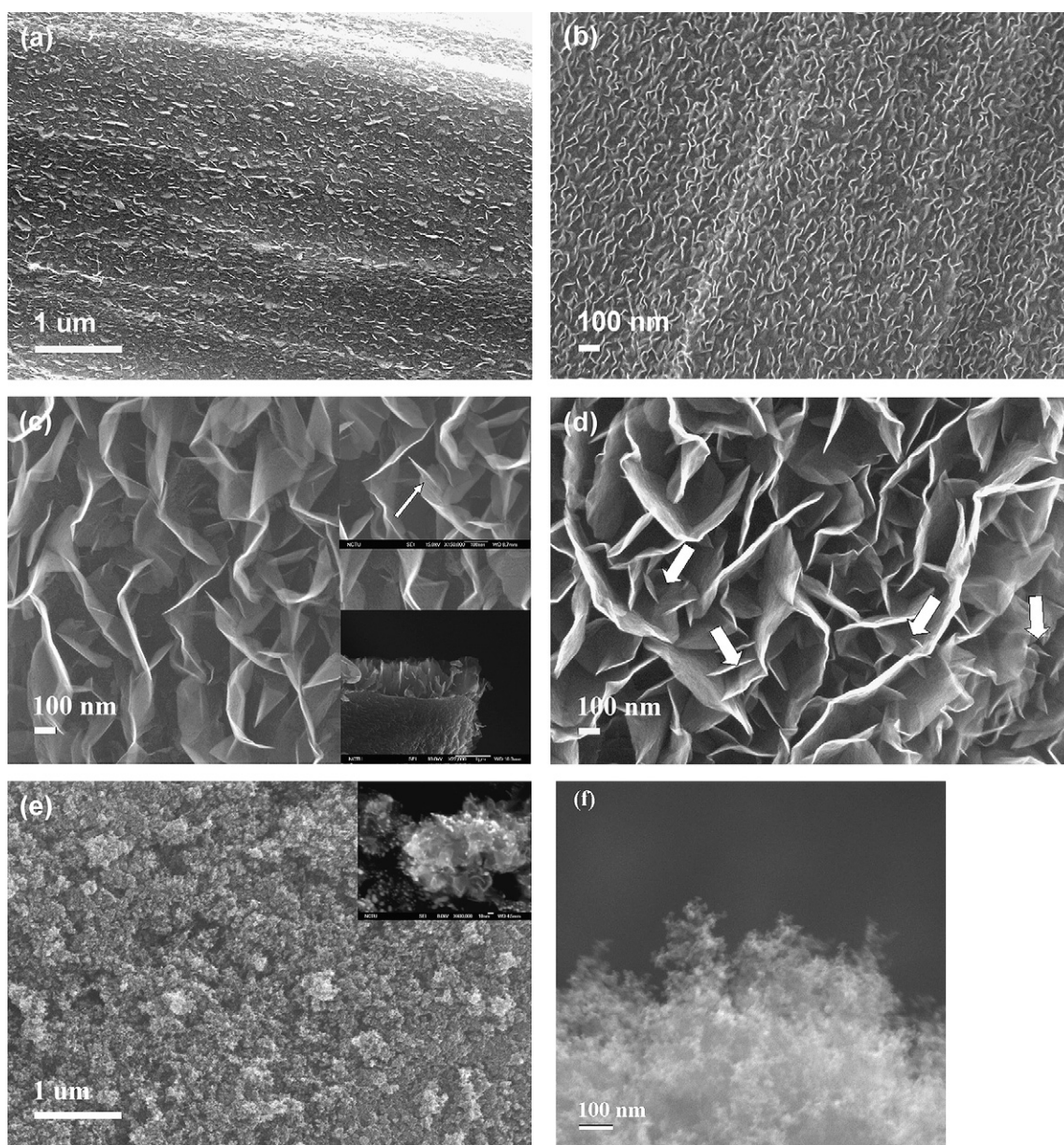


Fig. 1. SEM images of the structures formed on carbon cloth after H_2 plasma pretreatment and then CO_2/CH_4 treatment for (a) 5 min at 200 W, (b) 10 min at 200 W, (c) 15 min at 200 W (inset: cross-section image), (d) 15 min at 300 W, and (e) 15 min at 400 W (inset: high-magnification image of a flower-like aggregate); (f) 3D configuration of the sample prepared at 400 W.

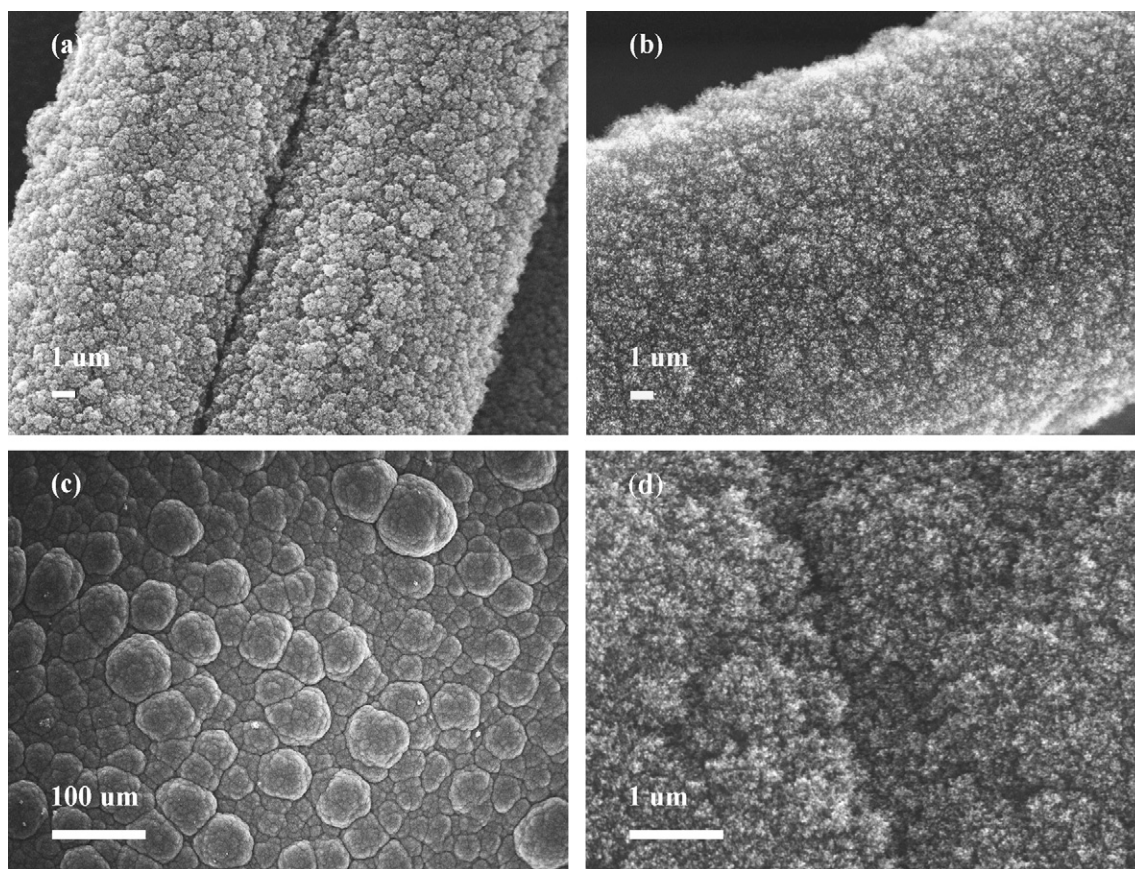


Fig. 2. SEM images of the samples deposited at 400 W for (a) 1 min, (b) 10 min, and (c, d) 30 min.

totally different morphology (Fig. 1(e)), however, when we applied an even greater microwave power (400 W) and relatively high substrate temperatures (up to 480 °C) to the system. Fig. 1(f) displays a 3D construction comprising flower-like aggregates of extremely small flakes. After 1 or 10 min of operation at 400 W, flower-like aggregates were deposited uniformly (Fig. 2(a) and (b), respectively). The diameter of each fiber, originally 8 μm, varied from 10 to 20 μm, corresponding to Fig. 2(a) and (b), respectively. The initial formation of the flower-like morphology at 400 W was different from initial structures formed at lower power. The growth rate was ca. 1 μm min⁻¹. Aggregates formed when we operated the system for a sufficiently long time—in our case, for 30 min (Fig. 2(c)). Even so, magnified image of the structure depicts the same aggregation, displayed in Fig. 2(d).

A critical microwave power is required for effective ion bombardment, sputtering, and etching during plasma processing [15], such that a disordered carbon structure can be formed. Even at a high deposition rate of carbon, the reaction time might not be sufficiently high for inner, disordered carbon atoms to form continuous walls through collision, leading to restricted graphitization. Our findings suggested that, at 400 W, an enormous number of amorphous carbon atoms deposited initially, impregnated with oxygen-containing groups as active sites, which then gradually transformed into CNF structures through aggregation and interior collision processes. The CNFs that we prepared in this study (20–30 nm long and 3–5 nm wide) are much smaller than those which have been limited as a 2D material [10,11]. Most interestingly, the 3D flower-like clusters prepared at 400 W had an average pore size of 12.3 nm and an appreciably greater surface

area (728.6 m²/g) than those prepared at 300 W (363.6 m²/g) or 200 W (331.3 m²/g). With respect to the structure formed at 200 W, the slightly increased surface area formed at 300 W resulted from the presence of stretching branches, consistent with our SEM observations. For comparison, the surface area of the unmodified carbon cloth was 119.5 m²/g.

The mechanism of synthesis of CNFs from carbon cloth can be divided broadly into three parts. At first, aggregation of carbon atoms occurs at the activated sites. The lateral growth of CNFs then proceeds in preference to vertical growth under the conditions; it results from the fact that dangling bonds of a free carbon atom can be considered asymmetric, with three in-plane sp² bonds and a p_z orbital that is perpendicular to this plane. This asymmetry is also an important factor for the catalytic synthesis of tubular structures. Finally, the carbon atoms are subjected to collision to form walls, as predicted by molecular dynamics simulations [16]. The deposition of a large amount of amorphous carbon and the bombarding and etching processes at high power may have led to the 3D construction. In addition, defects such as pentagons and heptagons may have led not only to the curved structures but also to the nanoflake branches, which are marked with arrows in Fig. 1, because they could serve as initiation sites for damaging of the surface. This process is common in the fabrication of CNTs [17].

Fig. 3 displays TEM images corresponding to the SEM images in Fig. 1. The thickness of each nanoflake was less than 5 nm. In contrast to the sample obtained at 400 W (Fig. 3(c)), which contained a greater amount of amorphous carbon, Fig. 3(a) and (b) reveals that continuous and ordered graphite layer structures formed at 200 and 300 W, respectively. In addition, a great

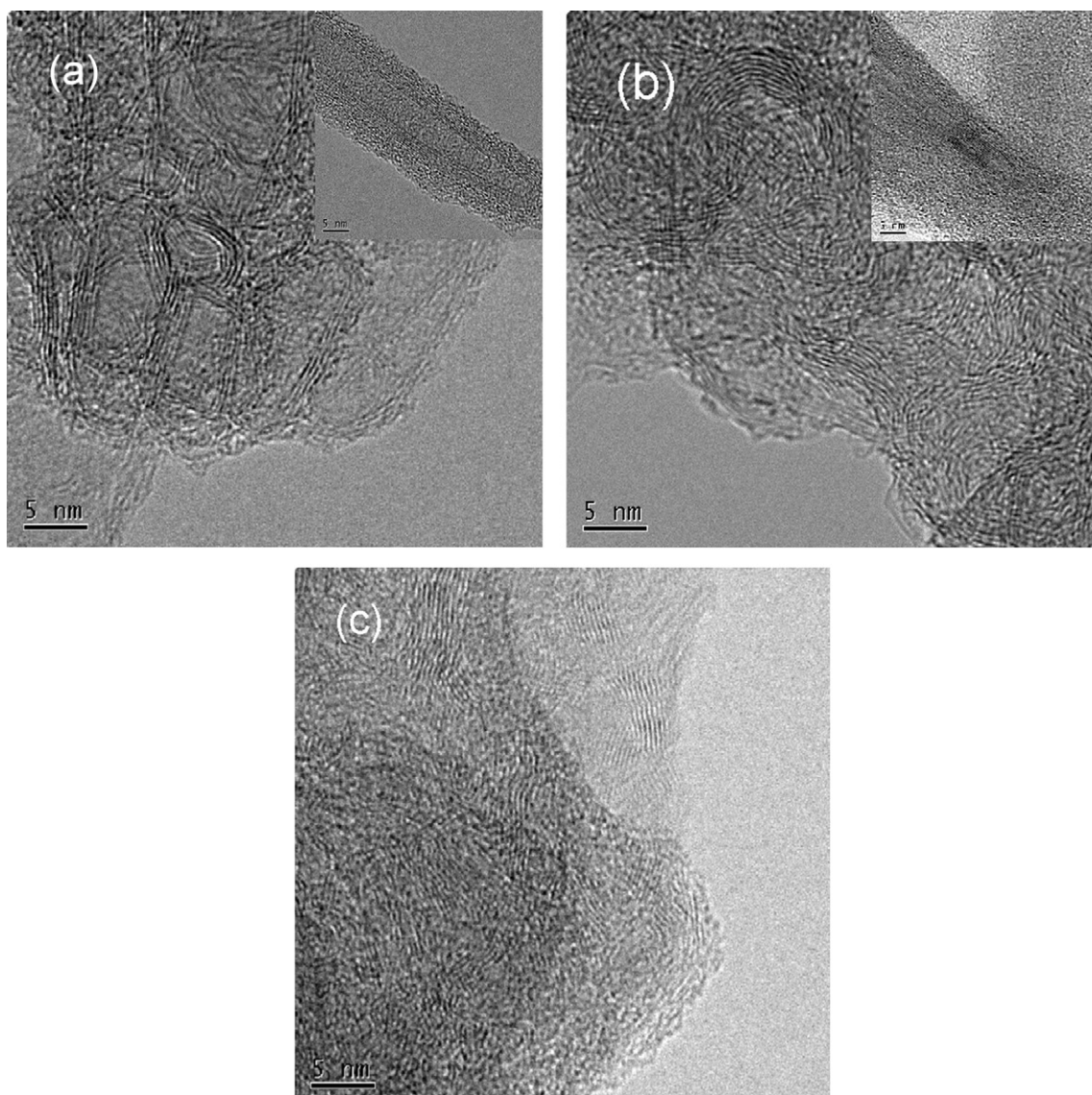


Fig. 3. TEM images of CNFs deposited (after H₂ plasma pretreatment) at microwave powers of (a) 200 W, (b) 300 W, and (c) 400 W.

curvature was present in the sample prepared at 200 W, as is evident in the inset of Fig. 3(a). The distance between pairs of graphitic planes in the nanoflakes was ca. 0.34 nm, which is consistent with that reported by Lin et al. [18]. When we applied a much higher microwave power of 500 W, we obtained an amorphous carbon film as a result of the intense impact of the bombarding and etching processes.

For the samples prepared without hydrogen pretreatment, Fig. 4 reveals that their structures were similar to those in Fig. 1. The major difference between these morphologies appeared at the beginning of the deposition process. Hydrogen pretreatment was more beneficial for forming uniformly active sites, leading to facile nucleation of carbon atoms for further synthesizing CNFs. There was a tendency to form non-crystalline structures in the absence of hydrogen pretreatment. A distinguishable difference between the investigation images in Figs. 1(d) and 4(d) depicts that the morphology of the sample prepared at 300 W in the absence of hydrogen pretreatment tends to exhibit the features similar to those of the sample prepared at 400 W after hydrogen pretreatment. This finding suggests that the initial stage at which the

carbon atoms nucleate as seeds is crucial to the resulting morphologies and structures. We recorded micro-Raman spectra to investigate this phenomenon.

Fig. 5 displays Raman spectra of the samples in the region 1200–1700 cm⁻¹. We observe three distinct peaks: a typical graphite vibration mode G-band at 1580 cm⁻¹, a disordered carbon mode D-band at 1348 cm⁻¹, and a D' line at 1620 cm⁻¹. The peak at 1580 cm⁻¹ indicates that graphite structures were fabricated during growth; the peak at 1348 cm⁻¹ resulted from defects in the curved graphite sheets, tube ends, and surviving impurities; the weak peak at 1620 cm⁻¹ corresponds to a maximum in the density of states of the mid-zone phonon and also reveals a disorder-induced behavior similar to that of the signal at 1348 cm⁻¹. We suggest that the D and D' lines resulted from disorder-induced features caused by lattice distortion [19].

Fig. 6 presents the ratio of the D-band integrating intensity (I_D) to the G-band integrating intensity (I_G) plotted with respect to the applied microwave power. The value of I_D/I_G was always greater than 2.0 because of the presence of defects (e.g., distortion, vacancies, and strain) in the graphite networks and to the more

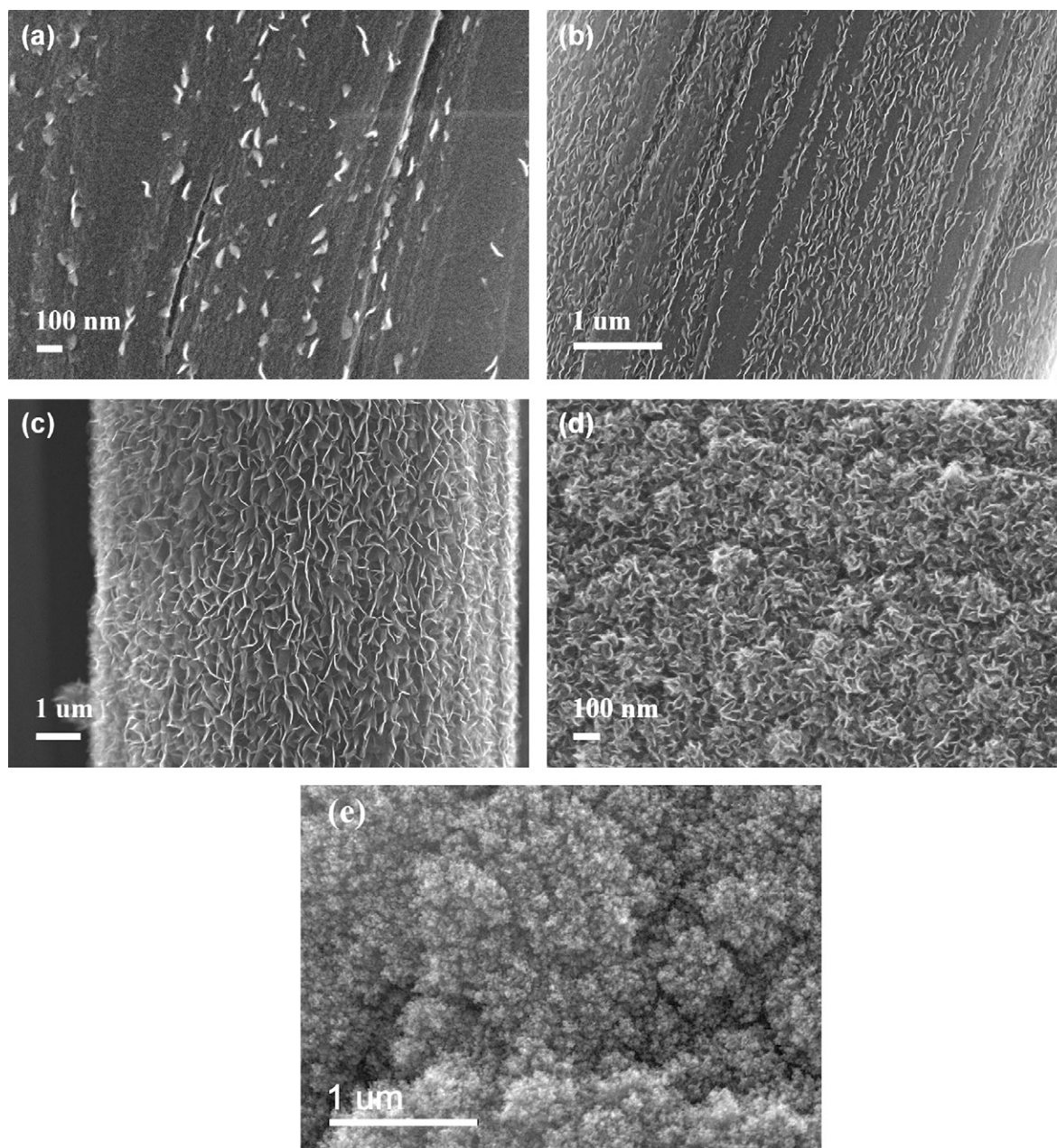


Fig. 4. SEM images of the samples deposited (without H₂ plasma pretreatment) through CO₂/CH₄ treatment for (a) 5 min at 200 W, (b) 10 min at 200 W, (c) 15 min at 200 W, (d) 15 min at 300 W, and (e) 15 min at 400 W.

nanocrystalline structure, especially for the growth process performed without catalyst. A recent Raman study revealed that higher values of I_D/I_G correspond to smaller grains [20]; this behavior is consistent with our TEM observation. We found that the value of I_D/I_G increased upon increasing the microwave power. This result is consistent with crystalline structures forming more readily at lower microwave powers. In addition, the values of I_D/I_G for the samples prepared after hydrogen plasma pretreatment were all less than those of the corresponding samples prepared without pretreatment. This behavior is consistent with the differences observed in the SEM images in Figs. 1(d) and 4(d). We suggest that a higher value of I_D/I_G is associated with the absence of carbon seeds at the onset of the fabrication process. Based on the influence of its functional groups, the carbon cloth

tends to be covered initially with amorphous carbon and then active sites containing functional groups such as COH and C=O are incorporated onto the surface [21]. These groups help to gather carbon atoms to form the so-called carbon seeds for the aggregation of carbon atoms. Therefore, the measured crystallinity would decrease as a result of the contribution from the amorphous carbon.

It is interesting to compare the properties of CNFs with CNTs because both are composed of graphitic planes. Nanoflakes exhibit stability similar to that of nanotube emitters for field emission applications and comparable field enhancement [22]. On the basis of the 3D porous structure and the high-surface area, we suspect that our CNFs might have potential applications in several fields, especially for energy storage systems.

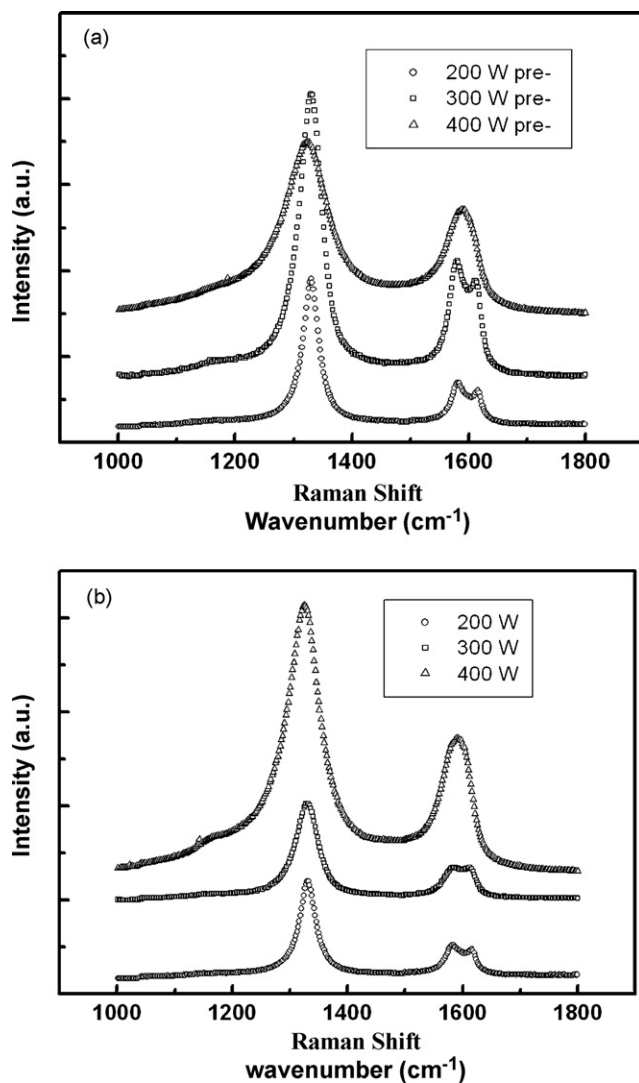


Fig. 5. Raman spectra of the CNFs deposited at 200, 300, and 400 W (a) after H_2 plasma pretreatment and (b) without H_2 plasma pretreatment.

4. Conclusion

We have used MPECVD at a low substrate temperature in a CO_2/CH_4 plasma system to fabricate 2D and 3D CNF structures. Because our fabrication technique is a catalyst-free process, the resulting materials do not require a purification prior to use. The applied microwave power had crucial influence on the degree of crystallization of the products. Microscopy and micro-Raman spectroscopic measurements revealed that highly ordered graphite structures were readily obtained at low power (200–300 W). The specific surface area of the 3D structure was almost double

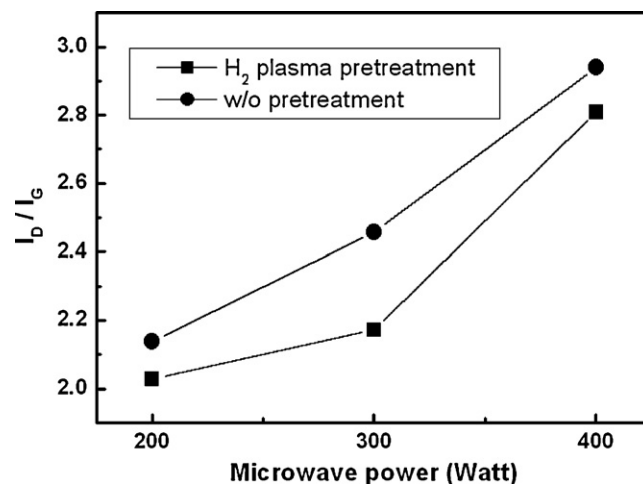


Fig. 6. Values of I_D/I_G from the Raman spectra plotted with respect to the applied microwave power.

that of the 2D structures because the 3D structure comprised an aggregate of many flower-like nanoflakes and, thereby, possessed a microporous structure. We suspect that our 3D CNF aggregate – prepared through a catalyst-free, low-temperature, highly efficient fabrication process – might have commercial applicability for use in energy storage systems because of its high-surface area and porous structure.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* 318 (1985) 162.
- [2] T.M. Whitney, J.S. Jiang, P.C. Searson, C.L. Chien, *Science* 261 (1993) 1316.
- [3] M.M.J. Treacy, T.W. Ebbenson, J.M. Gibson, *Nature* 381 (1996) 678.
- [4] P. Delaney, H.J. Choi, J. Ihm, S.G. Louie, M.L. Cohen, *Nature* 391 (1998) 466.
- [5] S.S. Wong, E. Joselevich, A.T. Woolley, C.L. Cheung, C.M. Lieber, *Nature* 394 (1998) 52.
- [6] S.J. Tans, A.R.M. Verschueren, C. Dekker, *Nature* 393 (1998) 49.
- [7] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, *Science* 286 (1999) 1127.
- [8] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassel, H. Dai, *Science* 283 (1999) 512.
- [9] D. Gournis, M.A. Karakassides, T. Bakas, N. Boukos, D. Petridis, *Carbon* 40 (2002) 2641.
- [10] G.H. Chen, W.G. Weng, D.J. Wu, C.L. Wu, J.R. Lu, P.P. Wang, X.F. Chen, *Carbon* 42 (2004) 753.
- [11] S.K. Srivastava, A.K. Shukla, V.D. Vankar, V. Kumar, *Thin Solid Film* 492 (2005) 124.
- [12] H. Keiser, K.D. Beccu, M.A. Gutjahr, *Electrochim. Acta* 12 (1976) 539.
- [13] Y.H. Wu, B.J. Yang, *Nano Lett.* 2 (2002) 355.
- [14] M. Chen, C.M. Chen, L.K. Wu, *J. Mater. Sci.* 37 (2002) 3561.
- [15] B. Chapman, *Glow Discharge Processes*, Wiley, 1996.
- [16] T. Kawai, Y. Miyamoto, O. Sugino, Y. Koga, *Phys. Rev. B* 66 (2002) 195409.
- [17] S.C. Mu, H.L. Tang, S.H. Qian, M. Pan, R.Z. Yuan, *Carbon* 44 (2006) 762.
- [18] C.R. Lin, C.H. Su, C.Y. Chang, C.H. Hung, Y.F. Huang, *Surf. Coat. Technol.* 200 (2006) 3190.
- [19] A.C. Ferrari, J. Robertson, *Phys. Rev. B* 61 (2000) 14095.
- [20] S. Kurita, A. Yoshimura, H. Kawamoto, T. Uchida, K. Kojima, M. Tachibana, P. Molina-Morales, H. Nakai, *J. Appl. Phys.* 97 (2005) 104320.
- [21] Z.L. Wang, Z.C. Kang, *Carbon* 35 (1997) 419.
- [22] J.M. Bonard, R. Gaal, S. Garaj, L. Thien-Nga, L. Forro, K. Takahashi, F. Kokai, M. Yudasaka, S. Iijima, *J. Appl. Phys.* 91 (2002) 10107.