

Thermal Conversion of Pine Wood Char to Carbon Nanomaterials in the Presence of Iron Nanoparticles

Sung Phil Mun Zhiyong Cai Fumiya Watanabe
Umesh P. Agarwal Jilei Zhang

Abstract

Southern yellow pine (*Pinus taeda*) wood char powder was thermally treated at 1,000°C in the presence of a 25-nm-size Fe nanoparticle catalyst. The thermally treated carbon powder materials were analyzed by Raman spectroscopy and high-resolution transmission electron microscopy. Well-aligned graphitic carbon structures with 15 to 17 layers on average were observed. These graphitic carbon structures were similar to those of graphite with an average interplanar distance of 0.34 nm. The Raman spectra results showed that the full-width half-maximum values of Raman G and D bands, and the peak intensity ratio, I_D/I_G , of thermally treated pine char after an acid purification treatment were 69 cm^{-1} , 126 cm^{-1} , and 0.16, respectively.

Man has historically used carbon materials for fuels, adsorbents, pigments, and iron smelting in daily life activities. New types of carbon materials such as carbon nanotubes (Iijima 1991), carbon-encapsulated metal nanoparticles (Tomita et al. 2000, Liu et al. 2002, Sano et al. 2003, Lu et al. 2005, Xu et al. 2006, El-Gendy et al. 2009, Sunny et al. 2010), carbon onions (Ugarte 1995), carbon nanohorns (Iijima et al. 1999), carbon microcoils (Motojima et al. 1990), and carbon nanorods (Wu et al. 2010) have been discovered. These carbon nanomaterials have attracted considerable attention in many industries because their special geometries and unique properties show great potential for application in nanoelectronic devices, energy storage, chemical probes, biosensors, field emission displays, magnetic data storage, xerography, and drug delivery (Hsin et al. 2008, Lu et al. 2010). Current methods to prepare such nanoparticles include arc discharge (Setlur et al. 1998), catalytic chemical vapor deposition (Flahaut et al. 2002, Liu et al. 2002), electron beam irradiation (Nishijo et al. 2005), high-temperature heat annealing (HTA; Tomita et al. 2000), and thermal pyrolysis (Sano et al. 2003). Of these methods, the HTA method has the potential to be scaled up for the commercial production of carbon nanomaterials because it is a simple and efficient method for high-volume production. Carbon sources that have been used for the synthesis of carbon nanomaterials include graphite, pitch, and carbon-containing compounds. There are limited studies on the use of lignocellulosic biomass as carbon sources (Lian and Wu 2009).

As fossil resources such as petroleum and coals are depleted, many efforts have been devoted to the develop-

ment of renewable and alternative resources of energy worldwide. Fast pyrolysis of lignocellulosic biomass for bio-oil production is one of the attempts extensively investigated since the 1980s. However, high production cost and conversion inefficiency are hindrances for commercialization of bio-oil production from lignocellulosic biomass (Bridgwater 2012). Wood char, a by-product from the fast pyrolysis of wood, accounts for 15 to 25 percent of the total products (Mohan et al. 2006). So far there is no good use for this by-product as a carbon source for producing other high value-added products except as a low-value fuel. The conversion of wood char into high value-added products can be one of the solutions to improve the economic feasibility of the pyrolysis process using lignocellulosic biomass. In this study, the feasibility of this undervalued wood char as a precursor to produce valuable

The authors are, respectively, Professor, Dept. of Wood Sci. and Technol., Chonbuk National Univ., Jeonju, Jeonbuk, South Korea (msp@chonbuk.ac.kr); Project Leader, USDA Forest Serv., Forest Product Lab., Madison, Wisconsin (zcaif@fs.fed.us); Director, Instrumentation Nanotechnology Center, Univ. of Arkansas, Little Rock (fxwatanabe@ualr.edu); Research Chemist, USDA Forest Serv., Forest Product Lab., Madison, Wisconsin (uagarwal@fs.fed.us); and Professor, Mississippi State Univ., Mississippi State (jzhang@cfr.msstate.edu [corresponding author]). Approved for publication as Journal Article no. FP 644 of the Forest and Wildlife Research Center, Mississippi State University. This paper was received for publication in March 2012. Article no. 12-00028.
©Forest Products Society 2012.

Forest Prod. J. 62(6):462-466.

carbon nanomaterials using a simple thermal treatment method was investigated. In addition, the effectiveness of Fe nanoparticles as a catalyst was studied.

Materials and Methods

Materials

Wood char particles used in this study were a by-product from the fast pyrolysis of loblolly pine (*Pinus taeda*) chips using an auger reactor operated at temperatures between 450°C and 550°C. The pine chips were prepared from No. 2 dried lumber obtained from a local lumber yard. Fe nanoparticles (FeNPs) were purchased from Sun Innovations Inc. (Fremont, California) with average particle size of 25 nm. Before being mixed with FeNPs, the wood char particles were ground with a pestle to submillimeter size and then passed through a Microfluidizer from Microfluidics (Newton, Massachusetts), first using a 200- μm chamber and then an 87- μm chamber about five times each. Scanning electron microscopy image analysis indicated that the final wood char powder size ranged from submicrometer to about 20 μm across.

Thermal treatment

The wood char powder was thermally treated in the presence of FeNPs as the catalyst. The thermal treatment was carried out in a split-hinge 1-inch quartz tube electric furnace (Mellen SC12R, 0.75X3) equipped with a temperature controller (Mellen PS 305-120-15-S1). The quartz tube had an outer diameter of 0.625 inch and a length of 19.75 inches. For each experimental run, 50 mg of FeNPs and 200 mg of char powder (1:4 by weight) were loaded into a porcelain boat and stirred. The boat was placed in the middle of the quartz tube. The mixture sample was heated to 1,000°C at a ramping rate of 20°C/min under an argon stream with a flow rate of 1 liter/min. The temperature was held at 1,000°C for 1 hour, the furnace was then turned off, and the sample was cooled to ambient temperature under argon atmosphere. The cooled sample was removed from the furnace and weighed to calculate the percentage of remaining carbon. Eight sample runs were prepared to produce thermally treated pine wood char with FeNPs (TPWC-Fe) and combined together for further analyses and purification.

Purification

A TPWC-Fe (0.614-g) sample and 5 mL of 25 percent nitric acid were placed in a 25-mL Erlenmeyer flask, and a 1.2-m glass tube as an air cooling condenser was attached to the flask. The flask was immersed into a PEG No. 400 bath set to 120°C and refluxed for 2 hours. The acid mixture was then transferred to a 125-mL Erlenmeyer flask using 50 mL of deionized (DI) water and then filtered through a nylon filter (1 μm). The residue on the filter was washed with 50 mL of DI water, and the washed residue was placed in a 125-mL Erlenmeyer flask using 50 mL of DI water. The 125-mL flask was boiled 1 hour. The mixture was refiltered using the nylon filter, and the residue on the filter was washed with 200 mL of DI water. The washed residue was transferred using DI water to a 25-mL beaker and dried on a hot plate. The residue remaining in the beaker was redried in a convection oven at 120°C overnight and then weighed to yield the acid-purified TPWC-Fe (A-TPWC-Fe).

Characterization

Raman spectroscopy characterized carbon structures of carbonaceous materials prepared in this study. Although the assignment of Raman bands typically appearing in the region 1,000 to 1,800 cm^{-1} is still controversial, it provides information on the molecular structure and chemical bonding of carbon atoms in carbonized materials (Yamauchi and Kurimoto 2003). In this study, Raman spectroscopy on wood char powder, TPWC-Fe, and A-TPWC-Fe samples was performed at room temperature using a Bruker RFS 100 spectrometer (Bruker Instruments Inc., Billerica, Massachusetts) equipped with a 1,064-nm 1,000-mW continuous wave diode pumped Nd:YAG laser. For high-resolution transmission electron microscopy (HRTEM), the wood char powder was further ground in ethanol by an agate mortar to reduce its size, and then a drop of the suspension was dripped onto carbon-coated copper grids. HRTEM analysis was performed on a JEM 2100F (F stands for Field Emission (Gun), JEOL, Japan) equipped with an EDAX (Ametek).

Results and Discussion

Carbonization yield and purification

Table 1 summarizes the carbonization yields of wood char powder after going through thermal and acid treatments. The yield of the char and FeNP mixture after the 1,000°C, 1-hour thermal treatment was 60.7 percent. Because the thermally treated char and FeNP mixture contains 20 percent FeNPs added as a catalyst, the amount of FeNPs was removed from the total weight of 250 mg in the calculation of the carbonization yield of wood char. After subtracting the FeNP weight of 50 mg, the calculated carbonization yield of the wood char was 50.9 percent. Thus, about 49 percent of wood char components were removed by the thermal treatment. In general, the carbonization yield of lignocellulosic biomass such as wood is reported to be less than 25 percent (Mun et al. 2002). In this study, the carbonization yield of 50.9 percent is high. This suggests that wood char could be a very good carbon source for the preparation of carbon-based materials.

Since thermally treated char materials contain noncarbon materials such as inorganic ash and FeNPs, the nitric acid solution of 25 percent was used to purify TPWC-Fe (Park et al. 2006). The carbon yield of TPWC-Fe after acid treatment was 41.7 percent (Table 1) because FeNPs and some amorphous carbons and inorganic materials were removed.

Raman spectroscopy

Figure 1 shows the Raman spectra of pine wood char, TPWC-Fe, and A-TPWC-Fe samples. Raman spectra of

Table 1.—Summary of carbon yields of thermally treated pine wood char before and after acid purification.^a

| | Value |
|---------------------------------|-------|
| Component weight (mg) | |
| Pine wood char | 200 |
| FeNPs | 50 |
| Before correcting for FeNPs (%) | 60.7 |
| After correcting for FeNPs (%) | 50.9 |
| After acid purification (%) | 41.7 |

^a FeNPs = Fe nanoparticles.

TPWC-Fe and A-TPWC-Fe samples consist of two main bands at 1,270 to 1,300 cm^{-1} (D band) and 1,590 to 1,600 cm^{-1} (G band), which are reported to be related to the vibration of sp^2 hybridized carbon bonded with structural imperfections and the in-plane vibration of sp^2 -bonded crystalline carbon, respectively (Ishimaru et al. 2007a, Sunny et al. 2010). The band for 1,500 to 1,550 cm^{-1} (D'' band) is associated with an amorphous sp^2 -bonded carbon (Ishimaru et al. 2007a).

The full-width half-maximum (FWHM) values of D and G bands, which are the differences between two wave numbers at half of the maximum peak intensity of either D or G bands for carbonaceous materials, are used to estimate the degrees of disorder and development of carbon crystallites, respectively (Ishimaru et al. 2001, 2007a, 2007b). It was reported that these two values become smaller with the increase in the degrees of order and development of carbon crystallites in carbonaceous materials. The D'' and G band peak intensity ratio, $I_{D''}/I_G$, is another parameter measuring the degree of carbonization occurring in carbonaceous materials. The values of $I_{D''}$ and I_G were calculated by drawing a baseline from 1,000 to 1,700 cm^{-1} first and then measuring the intensity values of the D'' and G bands

The wood char thermally treated in the presence of FeNPs clearly shows the Raman D and G bands (Fig. 1) compared with the char heated without FeNPs. The intensities of these two bands increased after TPWC-Fe was acid treated. This indicates that the method of thermally treating wood char in the presence of FeNPs and with acid purification is an effective way to increase the degrees of order and development of wood char carbon crystallites.

Table 2 summarizes the FWHM values of Raman D and G bands and the peak intensity ratio $I_{D''}/I_G$ of TPWC-Fe samples before and after acid purification. The A-TPWC-Fe sample had lower FWHM values of Raman D and G bands

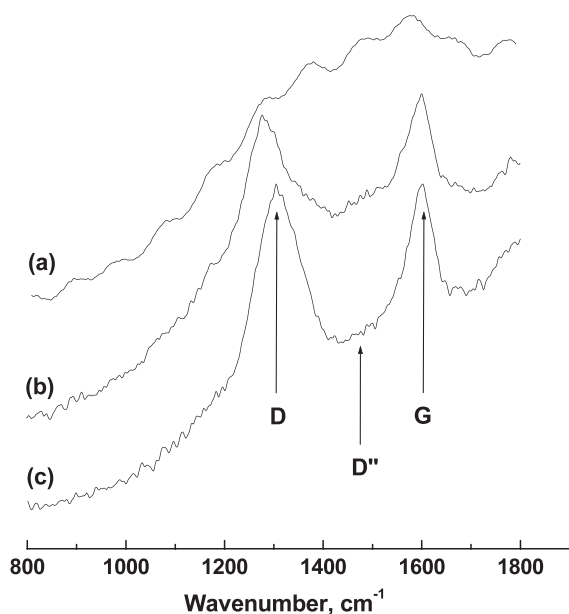


Figure 1.—Raman spectra of pine wood char (a) without heat treatment, (b) thermally treated pine wood char with Fe nanoparticles present (TPWC-Fe), and (c) acid-purified TPWC-Fe.

Table 2.—Results of Raman spectra analysis of thermally treated pine wood char with Fe nanoparticles (TPWC-Fe) and acid-purified TPWC-Fe (A-TPWC-Fe).^a

| Sample | FWHM of Raman G band (cm^{-1}) | FWHM of Raman D band (cm^{-1}) | $I_{D''}/I_G$ |
|-----------|---|---|---------------|
| TPWC-Fe | 83 | 144 | 0.39 |
| A-TPWC-Fe | 69 | 126 | 0.16 |

^a FWHM = full width half maximum.

than those values of the TPWC-Fe sample. The significant reduction of the peak intensity ratio $I_{D''}/I_G$ from 0.39 to 0.16 also was seen. These results indicate that the acid purification treatment was very effective in removing the amorphous phase of sp^2 -bonded carbon (Ishimaru et al. 2007b) and other impurities. For the A-TPWC-Fe sample, the FWHM values of Raman G and D bands and $I_{D''}/I_G$ were 69 cm^{-1} , 126 cm^{-1} , and 0.16, respectively, which are very close to those from the wood carbonization performed at 1,200°C without catalyst (Ishimaru et al. 2007b). This indicates that a similar degree of carbonization can be achieved at a lower temperature with the presence of FeNPs as a catalyst. Raman spectra analysis showed a possibility that the crystallites of carbon nanostructures were well developed and ordered in the A-TPWC-Fe sample.

HRTEM observation

Figures 2 and 3 show the typical HRTEM images of the A-TPWC-Fe sample. A typical HRTEM image (Fig. 2) of the A-TPWC-Fe sample shows that well-aligned and multilayered graphitic carbon structures appeared in thermally treated wood char in the presence of FeNPs. The formation of graphitic layers in this experiment is considered to be due to the graphitization of hydrocarbons from wood char during its heating at 1,000°C. Catalytic reactions between FeNPs and hydrocarbons from wood char lead to the formation of graphitic growth. This observation indicates that FeNPs play a role as a nucleus leading to the formation of the multilayered graphitic carbon structures rather than the carbon-shell-encapsulated FeNPs observed by Du et al. (2010) in an experiment of heating the same pine char but preimpregnated with iron nitrate solution.

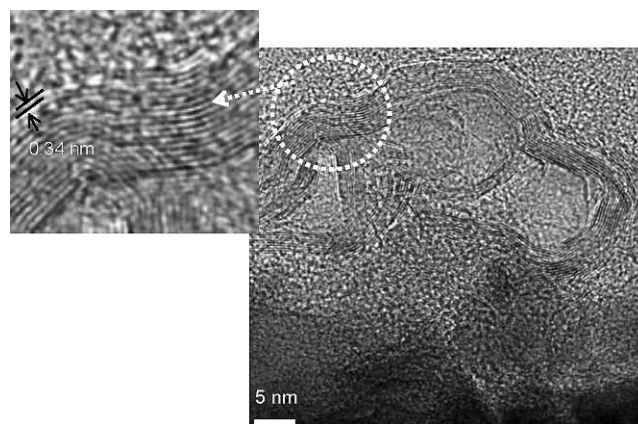


Figure 2.—High-resolution transmission electron microscopy images of acid-purified thermally treated pine wood char with Fe nanoparticle samples showing well-aligned and multilayered graphitic carbon structures.

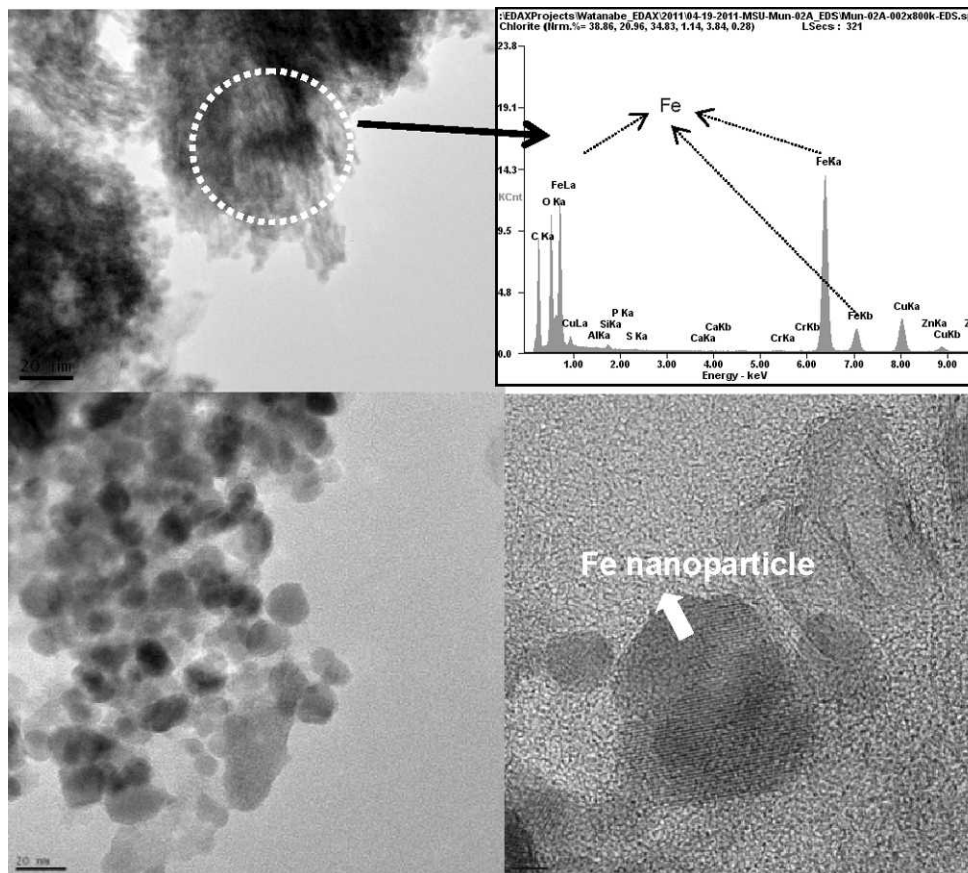


Figure 3.—High-resolution transmission electron microscopy images and energy dispersive X-ray spectrum of acid-purified thermally treated pine wood char with Fe nanoparticle samples.

Transition metals such as Fe, Ni, and Co are well-known catalysts for the production of carbon nanotubes and nanomaterials (Cho et al. 1996, Journet and Bernier 1998). These results indicated that different carbon nanostructures can be produced using different states of iron as catalysts such as solid particles or liquid phase. This seems to be the catalyst particle size effect. The atomic radius of iron in the iron(III) nitrate solution is only 0.0785 nm, while in the solid catalyst used in this study, the Fe particle size averaged 25 nm in diameter. A high magnification image (Fig. 2) of the multilayered graphitic carbon structure shows that the structure consists of 15 to 17 layers, and the interlayer spacing of the graphitic layers is about 0.34 nm, which is close to that in the graphite (002) plane.

It was noticed (Fig. 3) that the FeNPs were still observed by the HRTEM and also detected by energy dispersive X-ray spectrometry in the A-TPWC-Fe sample even after it went through 25 percent HNO₃ treatment and without carbon shells around the FeNPs being observed under HRTEM (Fig. 3). This indicated that these FeNPs might be encapsulated in an amorphous carbon matrix or disordered graphitic layers that were not observed through HRTEM, which protected Fe from being removed by acid washing. Lu et al. (2005) also reported that amorphous carbon-encapsulated Fe nanoparticle (Fe-C core-shell) structures still remained after ultrasonification in 10 M HNO₃ for 20 minutes and refluxing for 6 hours.

Conclusions

The pine wood char powder as a carbon precursor and FeNPs as a catalyst were mixed and thermally treated at 1,000°C for 1 hour and then acid purified. The FeNPs allowed the formation of well-aligned graphitic carbon structures with 15 to 17 layers on average. The average interlayer spacing of the multilayered graphitic carbon structure observed in this study was about 0.34 nm, which is close to that of the graphite (002) plane structure. Nanostructures of carbon materials prepared from wood char can be altered by the state of catalysts used in the heat-treated process such as solid particles or liquid phase.

Acknowledgment

This work is supported by the USDA Forest Service through grant 11JV111112409711121332 (J. Zhang).

Literature Cited

- Bridgwater, A. V. 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 38:68–94.
- Cho, W. S., E. Hamada, Y. Kondo, and K. Takayanagi. 1996. Synthesis of carbon nanotubes from bulk polymer. *Appl. Phys. Lett.* 69(2):278–279.
- Du, Y., C. Wang, H. Toghiani, Z. Cai, X. Liu, J. Zhang, and Q. Yan. 2010. Synthesis of carbon-encapsulated metal nanoparticles from wood char. *Forest Prod. J.* 60(6):527–533.
- El-Gendy, A. A., E. M. M. Ibrahim, V. O. Khavrus, Y. Krupskaya, S. Hampel, A. Leonhardt, B. Büchner, and R. Klingeler. 2009. The synthesis of carbon coated Fe, Co and Ni nanoparticles and an examination of their magnetic properties. *Carbon* 47:2821–2828.

- Flahaut, E., F. Agnoli, J. Sloan, C. O'Connor, and M. L. H. Green. 2002. CCVD synthesis and characterization of cobalt-encapsulated nanoparticles. *Chem. Mater.* 14:2553–2558.
- Hsin, Y. L., C. F. Lin, Y. C. Liang, K. C. Hwang, J. C. Horng, J. A. A. Ho, C. C. Lin, and J. R. Hwu. 2008. Microwave arcing induced formation and growth mechanisms of core/shell metal/carbon nanoparticles in organic solutions. *Adv. Funct. Mater.* 18(14):2001–2034.
- Iijima, S. 1991. Helical microtubules of graphitic carbon. *Nature* 354:56–58.
- Iijima, S., M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, and K. Takahashi. 1999. Nano-aggregates of single-walled graphitic carbon nano-horns. *Chem. Phys. Lett.* 309:165–170.
- Ishimaru, K., T. Hata, P. Bronsveld, D. Meier, and Y. Imamura. 2007a. Spectroscopic analysis of carbonization behavior of wood, cellulose and lignin. *J. Mater. Sci.* 42:122–129.
- Ishimaru, K., T. Hata, P. Bronsveld, T. Nishizawa, and Y. Imamura. 2007b. Characterization of sp²- and sp³-bonded carbon in wood charcoal. *J. Wood Sci.* 53:442–448.
- Ishimaru, K., T. Vystavel, P. Bronsveld, T. Hata, Y. Imamura, and J. D. Hosson. 2001. Diamond and pore structure observed in wood charcoal. *J. Wood Sci.* 47:414–416.
- Journet, C. and P. Bernier. 1998. Production of carbon nanotubes. *Appl. Phys. A* 67:1–9.
- Lian, K. and Q. Wu. 2009. Carbon-encased metal nanoparticles and sponges, methods of synthesis, and methods of use. US patent 2009/0098033 A1. April 16, 2009.
- Liu, B. H., J. Ding, Z. Y. Zhong, Z. L. Dong, T. White, and J. Y. Lin. 2002. Large-scale preparation of carbon-encapsulated cobalt nanoparticles by the catalytic method. *Chem. Phys. Lett.* 358:96–102.
- Lu, B., H. Huang, X. L. Dong, and J. P. Lei. 2010. Catalytic pyrogenation synthesis of C/Ni composite nanoparticles: Controllable carbon structures and high permittivities. *J. Phys. D Appl. Phys.* 43:105403. DOI:10.1088/0022-3727/43/10/105403.
- Lu, Y., Z. Zhu, and Z. Liu. 2005. Carbon-encapsulated Fe nanoparticles from detonation-induced pyrolysis of ferrocene. *Carbon* 43:369–374.
- Mohan, D., C. U. Pittman, Jr., and P. H. Steele. 2006. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuels* 20(3):848–889.
- Motojima, S., M. Kawaguchi, K. Nozaki, and H. Tawanaga. 1990. Growth of regularly coiled carbon filaments by Ni catalyzed pyrolysis of acetylene, and their morphology and extension characteristics. *Appl. Phys. Lett.* 56:321–323.
- Mun, S. P., U. D. Hwang, S. B. Park, and S. D. Kwon. 2002. Characterization of pine bark charcoal prepared from small and large-scale carbonization kilns. *Korea Forestry Energy* 21(2):1–9.
- Nishijo, J., C. Okabe, J. Bushiri, K. Kosugi, N. Nishi, and H. Sawa. 2005. Formation of carbon-encapsulated metallic nano-particles from metal acetylides by electron beam irradiation. *Eur. Phys. J. D* 34(1–3):219–222.
- Park, T. J., S. Banerjee, T. Hemraj-Benny, and S. S. Wong. 2006. Purification strategies and purity visualization techniques for single-walled carbon nanotubes. *J. Mater. Chem.* 16:141–154.
- Sano, N., H. Akazawa, T. Kikuchi, and T. Kanki. 2003. Separated synthesis of iron-included carbon nanocapsules and nanotubes by pyrolysis of ferrocene in pure hydrogen. *Carbon* 41:2159–2162.
- Setlur, A. A., J. Y. Dai, J. M. Lauerhaas, and R. P. H. Chang. 1998. Formation of filled carbon nanotubes and nanoparticles using polycyclic aromatic hydrocarbon molecules. *Carbon* 36(5–6):721–723.
- Sunny, V., D. Sakthi Kumar, Y. Yoshida, M. Makarewicz, W. Tabiś, and M. R. Anatharaman. 2010. Synthesis and properties of highly stable nickel/carbon core/shell nanostructures. *Carbon* 48:1643–1651.
- Tomita, S., M. Hikita, M. Fujii, S. Hayashi, and K. Yamamoto. 2000. A new and simple method for thin graphitic coating of magnetic-metal nanoparticles. *Chem. Phys. Lett.* 316:361–364.
- Ugarte, D. 1995. Onion-like graphitic particles. *Carbon* 33(7):989–993.
- Wu, B., H. Song, J. Zhou, and X. Chen. 2010. Formation mechanism of carbon-encapsulated iron nanorods in a co-carbonization process. *Carbon* 49(3):890–894.
- Xu, B., J. Guo, X. Wang, X. Liu, and H. Ichinose. 2006. Synthesis of carbon nanocapsules containing Fe, Ni or Co by arc discharge in aqueous solution. *Carbon* 44:2631–2634.
- Yamauchi, S. and Y. Kurimoto. 2003. Raman spectroscopic study on pyrolyzed wood and bark of Japanese cedar: Temperature dependence of Raman parameters. *J. Wood Sci.* 49:235–240.