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Carbon nanofibers synthesized by pyrolysis of chloroform and ethanol mixture

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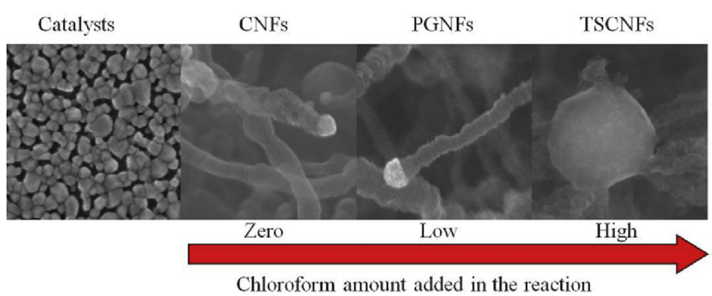
HIGHLIGHTS

- The morphology of CNFs changed while different amount of $CHCl_3$ presented.
- The interaction of Ni and Cl changed the geometry and morphology of catalysts.
- The structure of CNFs formed attributed to the surface morphology of catalysts.
- PGNFs and TSCNFs were perpendicular and random stacking of graphene.

GRAPHICAL ABSTRACT



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ABSTRACT

Platelet graphite nanofibers (PGNFs) and turbostratic carbon nanofibers (TSCNFs) were synthesized by the pyrolysis of 3 and 10 vol% chloroform in ethanol, respectively, in the presence of Ni catalyst at 700 °C. Auger electron spectrometry analysis reveals that the participation of chloroform in the synthesis led to Ni–Cl bonding on the surface of the catalysts, resulting in a relatively poor crystalline layer and a coarse surface. Furthermore, the Ni–Cl compound affected the melting point and mobility of Ni, changing the morphology and geometrical shape of Ni particles. A low amount of chlorine in the catalyst led to the formation of smaller catalyst particles with a flat surface, resulting in graphene nanosheets stacked perpendicular to the fiber axis, which became PGNFs. In contrast, a high amount of chlorine in the catalyst led to the aggregation of the catalyst and thus the formation of large catalyst particles with a rough surface, resulting in the random stacking of graphene nanosheets, which became TSCNFs. The participation of chlorine was found to be important in the synthesis of the PGNFs and TSCNFs.

1. Introduction

Fibrous carbon nanomaterials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted a lot of attention due to their unique crystalline structure as well as excellent physical and chemical properties. A wide variety of applications, such as gas sensors [1,2], electrodes [3–5], field-emission devices [6,7], adsorption materials [8,9], quantum wires [10–12], and gas storage [13–17], have been reported.

CNFs are synthesized mainly using catalytic chemical vapor deposition (CCVD) [18–22]. CCVD is an efficient method for production as it allows the control of synthesis parameters such as

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reaction temperature, carbon source, and type of catalyst. The decomposition of a carbon source (CO, CH_4, or C_2H_2) on catalysts (Fe, Co, Ni, or their alloys) allows a solid solution of metal carbides to form. Excess carbon atoms in the metal carbide diffuse out from the catalyst to form CNFs. In several recent reports, ethanol was found to be an attractive precursor for the synthesis of CNTs and CNFs. Maruyama et al. [23,24] fabricated single-wall CNTs from ethanol vapor at relatively low temperatures and reduced pressures. Red'kin et al. [25] reported that the ethanol molecules decompose into simpler species, such as CH_4, CO, and H_2, which are involved in the growth of CNFs of various thicknesses or CNTs on Ni catalysts. BaO et al. [26] synthesized CNFs at atmospheric pressure by ultrasonic spray pyrolysis of ethanol without a catalyst.

Several types of fibrous carbon nanomaterial, such as CNTs [27,28], CNFs [29–33], and metal-filled CNTs [34–37], have been fabricated using a chlorine-containing compound as a promoter in the reaction environment. The morphology and characteristics of fibrous carbon nanomaterials strongly depend on the shape and properties of the catalyst, which are greatly affected by process temperature [18,38]. In addition to the effect of temperature, the participation of halide in the synthesis changes the properties of catalysts, such as the melting point, topography, particle size, and geometrical shape [39,40], and thus determines the type of fibrous carbon nanomaterial formed.

In this study, CNFs were synthesized by pyrolysis of a mixture of ethanol and chloroform. CCVD was conducted using a chloroform/ethanol mixture as the carbon source and Ni as the catalyst. The ratio of the mixture was varied to determine the effect of chlorine on the morphological changes of the catalyst and CNFs. The interactions of Cl, Ni, and C elements were also studied.

2. Experimental details

CNFs were prepared by pyrolysis of an ethanol and chloroform (purity 99.99%, ECHO) mixture with Ni employed as the catalyst. The catalyst was prepared as follows. 0.5 M nickel(II) acetate (purity 99%, Showa) as the Ni catalyst precursor and 0.5 M monoethanolamine (purity 99.7%, J.T. Baker) were dissolved and well mixed in 2-methoxyethanol (purity 99%, Alfa Aesar) at 60 °C until the solution became translucent green. The solution was spin-coated onto a silicon chip and thermally treated for 30 min at 700 °C in air. For CNF synthesis, the chip with catalysts was placed in the middle of a tubular furnace. The inert gas was admitted into the reactor while the furnace was heated to 700 °C from room temperature at a rate of 15 °C/min. A mixture of chloroform and ethanol with ratios of 0, 3, and 10 (v/v) was loaded in a round-bottom flask. At the reaction temperature, 100 sccm of H_2 with chloroform and ethanol was introduced into the quartz tube for 20 min to synthesize CNFs. The concentrations of chloroform and ethanol were about 36 ppm and 22 ppm, respectively, for the ratio of 3 (v/v) while that of chloroform and ethanol were about 170 ppm and 20 ppm, respectively, for the ratio of 10 (v/v). The schematic of the reaction apparatus is shown in Fig. 1.

The morphology of the CNFs was observed with a field-emission scanning electron microscope (SEM, Hitachi S-4800) and the crystal structure was examined with a high-resolution transmission electron microscope (HR-TEM, JEOL JEM 2010). A Raman scattering spectrometer (Horiba XploRA) was used to determine the relative intensity of the G-band and D-band in the spectrum. The relative content of elements and functional groups on CNFs was characterized by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI Quantera SXM). The mainly qualitative analysis of elements present on the specimen surface was conducted using an Auger electron spectrometer (AES, ULVAC-PHI PHI 700).

3. Results and discussion

The experiments were conducted with mixtures of ethanol and chloroform for the synthesis of CNFs. Fig. 2(a) and (b) show SEM images of the materials synthesized using ethanol as a carbon source with and without H_2 reduction treatment at 700 °C for 10 min prior to synthesis, respectively. Fig. 2(a) shows that the CNFs were about 40 nm in diameter and a few μm in length. The morphology of these CNFs is similar to that reported by Red'kin et al. [25], who also used Ni as a catalyst and ethanol as a carbon source but a different method of preparing the catalyst. The filament materials obtained in their study were CNFs or CNTs with various thicknesses. Ethanol decomposed into species such as CH_4, CO, and H_2 [25]. In the presence of Ni catalyst, carbon nanomaterials can form. When the reduction treatment was omitted, the formed materials had a rough surface and irregular, short, and string-like structures, as shown in Fig. 2(b). The structure and morphology of the formed materials were very different from those obtained with H_2 reduction treatment. It is believed that activation of Ni catalyst by H_2 reduction plays an important role in the formation of CNFs. The shape and properties of the catalyst determine the type of obtained fibrous carbon nanomaterial [18]. Fig. 3 shows SEM and high-resolution SEM (HR-SEM) images of CNFs fabricated by pyrolysis from a mixture of chloroform and ethanol without H_2 reduction treatment. Fig. 3(a) shows CNFs synthesized by pyrolysis of 3 vol% chloroform in ethanol as the carbon source. As can be seen, the catalyst particles were on the top of the fibers, which suggest a top-growth mechanism. In addition, comparing to the material synthesized by ethanol (no chloroform) shown in Fig. 2(b), it is clear that the chloroform activated the catalysts for the formation of the CNFs. Fig. 3(b) shows a CNF with a hemispherical catalyst on the tip. The CNF, with a zigzag-like shape, grew from the flat surface of the catalyst. These CNFs are classified as platelet graphite nanofibers (PGNFs) [30]. Fig. 3(c) and (d) shows CNFs synthesized by pyrolysis of 10 vol% chloroform in ethanol as the carbon source. As can be seen, with an increased amount of chloroform, the catalysts aggregated to become larger particles with an irregular shape and rough surface [33]. Many CNFs grew from a single catalyst and the CNFs were porous, curly, and not well crystalline. These CNFs are classified as turbostratic CNFs (TSCNFs) [31]. It is believed that the amount of chlorine involved in the reaction affects the growth mechanism of the CNFs [33,41]. When the chloroform ratio in the carbon source mixture was increased, the morphology of the CNFs changed. These two types of CNF are similar to those obtained in our previous study, which used a high concentration of $HCl_{(aq)}$ as an additive in the polymer carbon source [33]. Wu et al. [42] reported that the major products from the decomposition of chloroform include hydrocarbons and chlorine-containing compounds such as CH_4, C_2H_4, C_2H_6, CH_2Cl_2, CH_3Cl, C_2Cl_4, and HCl. These gaseous species are different from those decomposed from ethanol. The morphologies of the as-produced materials can be attributed to the effects of temperature [31] and chlorine-containing compounds [33]. The compounds reacted with Ni particles during the synthesis of CNFs at high temperature. Yasuo [39] reported that chlorine diffused into Ni particles to form the Ni–Cl compound during thermal treatment using HCl. The Ni–Cl compound affected the melting point and the mobility of Ni, resulting in changes in the morphology and geometrical shape of Ni particles [40]. It is well known that the shape of the catalyst determines the morphology of CNFs [18,38].

Fig. 4 shows TEM and HR-TEM images of a PGNF and a TSCNF. Fig. 4(a) shows a TEM image of a PGNF with a catalyst in the tip of the fiber. The interface of the CNF and the catalyst is a flat surface. The HR-TEM image in Fig. 4(b) reveals that the PGNF had a good arrangement of graphene nanosheets packed perpendicular to the