

Synthesis and Purification of Carbon Nanofibers Prepared Using a Nickel-Alumina Catalyst Derived from Feitknecht Compound

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1. Introduction

Since the discovery of Iijima in 1991 [1], carbon nanotubes (CNTs) have been an attractive new material due to its unique properties. Owing to these outstanding physical and chemical properties, CNTs show the great potential of following applications, such as a field emission source [2-10], hydrogen storage material [11-16], etc. The graphite basal planes of CNTs are arranged parallel to the fiber axis. However, the carbon nanofibers (CNFs) can be produced with graphite platelets arranged parallel, perpendicular, or at an angle with respect to the fiber axis. These three types of graphite platelet arrangement are designated as “tubular”, “platelet” and “herringbone”, respectively [15]. It has been reported that the exposed edge of graphite basal plane is ideal for gas sorption, and the d-spacing of graphite platelet is larger than 3.35 Å, an ideal configuration for the storage of hydrogen, whose kinetic diameter is only 2.89 Å [15]. Chambers *et al.* has reported that the CNFs with platelet and herringbone structure show better hydrogen storage ability than those with tubular structure [15].

Clays are characterized by a layered structure. Feitknecht compound (FC) was found as a natural layered clay, which has been used as the precursor of catalyst for steam reforming since 1970s. It has been proved that FC is a catalyst with high activity for many reactions [17]. FC structure is also called hydrotalcite-like structure. This kind of structure contains octahedrally coordinated trivalent (Al^{3+} , Fe^{3+}) and bivalent (Ni^{2+} , Co^{2+}) cations and the interlayer anions (CO_3^{2-} , SO_4^{2-} , NO_3^{2-}). The trivalent and the bivalent cations distribute randomly in octahedral coordinates. The catalyst property can be modified easily by calcination conditions and the selection of cations. After calcination, FC will lose interlayer anions and form well-mixed oxide [18,19]. With proper reduction process, a paracrystalline metal phase will form and the particle size of the metal could be only several nanometers, that leads to high and stable catalysis activity.

Catalytic growth of CNFs usually uses a transition metal or alloy as the catalyst. The deposition temperature of CNFs is near the melting point of metal catalyst. Due to the high temperature thermal decomposition of hydrocarbon will happen, and non-catalytic carbon deposition will be found. These carbons come from thermal decomposition of hydrocarbon and have different structures and properties. The deposition temperature of CNFs is lower with Ni catalyst. However, it has been reported that the length of CNFs is shorter with Ni catalyst than either Co or Fe catalyst [20], and the deactivation of Ni catalyst is easier [21].

In this experiment, FC was used as the precursor of Ni-Al₂O₃ catalyst for catalytic growth of CNFs. Catalytic chemical vapor deposition of CNFs was carried out at different temperatures. The carbon yield and graphite platelet arrangement of CNFs that deposited at different temperatures will be studied. TGA, X-ray diffraction (XRD) and XPS were used to evaluate the effect of purification process including HCl de-catalyst and H₂O₂ oxidation for removing amorphous carbons.

2. Experimental

2.1. Preparation of catalyst precursor

Catalyst precursors were synthesized by coprecipitation of Ni(NO₃)₂•6H₂O and Al(NO₃)₃•9H₂O in a certain proportion with a total concentration of metal ions of 1 mol/l. Na₂CO₃ with a concentration of 1.0 mol/l was used as precipitate. The precipitates were washed with DI water to remove the sodium ions, then dried at 120 °C for 24 h and calcined at 500°C for 10 h. The powders thus formed were crushed and sieved into particles with a particle size of 325-400 mesh.

2.2. Growth of CNFs

The gas mixture of CH₄/N₂ or CH₄/H₂ was used as reactant for catalytic growth of CNFs. The total flow rates of CH₄/N₂ and CH₄/H₂ were 45 ml/min and 100 ml/min, respectively. The catalyst powders were reduced at 973 K with a N₂/H₂ atmosphere of N₂:H₂=3:1 for 30 min, then the furnace was cooled down to the deposition temperature of CNFs. The depositions were carried out at a temperature interval ranged from 723 K to 973 K for 3 h. The CNFs grown at 823 K and 873 K were then graphitized at 2673 K.

2.3. Purification of CNFs

The catalysts in CNFs were removed by hydrochloric ultrasonic bath. CNFs were immersed in HCl solution with a concentration of 3 M for 24 h. The amorphous carbon was removed by hydrogen peroxide at 338 K for 48 h.

2.4. Characterization

The morphology and microstructure of CNFs were characterized by SEM, XRD and TEM. The effects of purification process and graphitization treatment were evaluated by TGA, XRD and ESCA.

3. Results and discussion

3.1. Catalyst characteristics

Fig. 1 shows the XRD pattern of co-precipitated, calcined and reduced FC samples with the ratio of Ni²⁺/Al³⁺=3:1. As shown in Fig. 1(a), the co-precipitated sample is the Feitknecht compound, and there is only NiO phase after calcination (Fig. 1(b)). When the Ni²⁺/Al³⁺ ratio was decreased to 3/7, the calcination causes FC to form a phase near to NiO. There is no Al₂O₃ peak even the Ni²⁺/Al³⁺ ratio was decreased from 3/1 to 3/7. A similar result was also obtained by Li *et al.* [21]. Both Ni and NiO peaks were

observed after reduction in a N_2/H_2 atmosphere (Fig. 1(c)). The catalysts with both ratios of Ni^{2+}/Al^{3+} (3/1 and 3/7) were used for the catalytic growth of CNFs. The results indicated that the yield of CNFs depends only on Ni^{2+} amount.

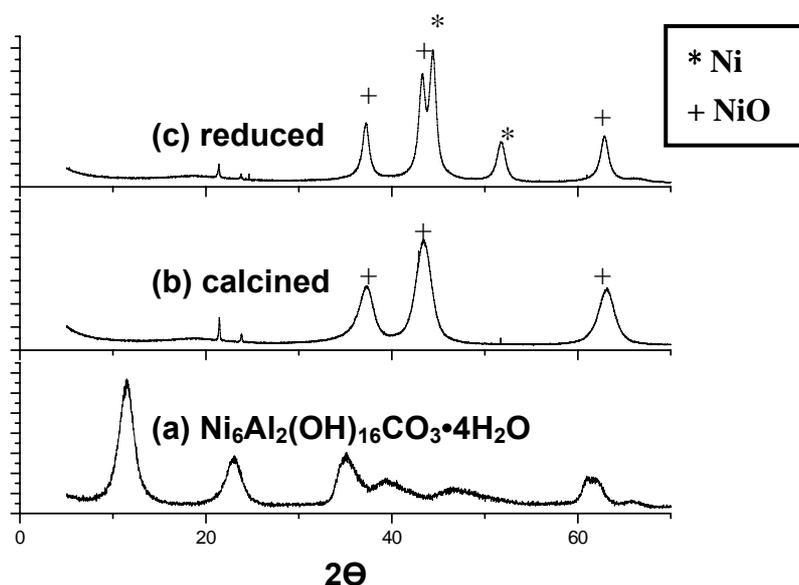


Fig. 1. XRD patterns of (a) Feitknecht compound, (b) calcined FC, and (c) reduced FC.

3.2. Growth and purification of CNFs

3.2.1 Composition of reactants and deposition temperature

Fig. 2 shows the relationship between carbon yield and deposition temperature for both CH_4/N_2 and CH_4/H_2 reactants. The carbon yield was calculated as the ratio of the weight of carbon products (including CNF and amorphous carbon) and the weight of catalyst used. As indicated in Fig. 2, the carbon yield increases with growth temperature up to 873 K for the CH_4/N_2 reaction atmosphere, and a maximum yield of 14.5 was achieved. The carbon yield decreases significantly at 923K as a consequence of rapid deactivation of catalyst. Fig. 3 shows the morphology of CNFs synthesized at different growth temperatures. It is noted that CNFs with a smaller diameter were synthesized while the deposition temperature increased from 823 K to 873 K.

Hydrogen is a necessary reactant of CNFs synthesized in many cases. However, hydrogen acts as a retardant of CNFs growth in this case. As shown in Fig.2, higher reaction temperature is required for the growth of CNFs, and much lower carbon yield was obtained when the CH_4/H_2 reaction atmosphere was used. Fig. 4 shows the morphology of CNFs synthesized using the CH_4/H_2 atmosphere. CNFs were grown only above 973K. Large amount of non-fiber deposits could be observed and the diameter and morphology of CNFs were much less uniform. The carbon yield at 1073 K and 1173 K were very close to that at 973 K (Fig.2). However, SEM photographs show that the primary deposit is soot when the deposition temperature is above 1073K.

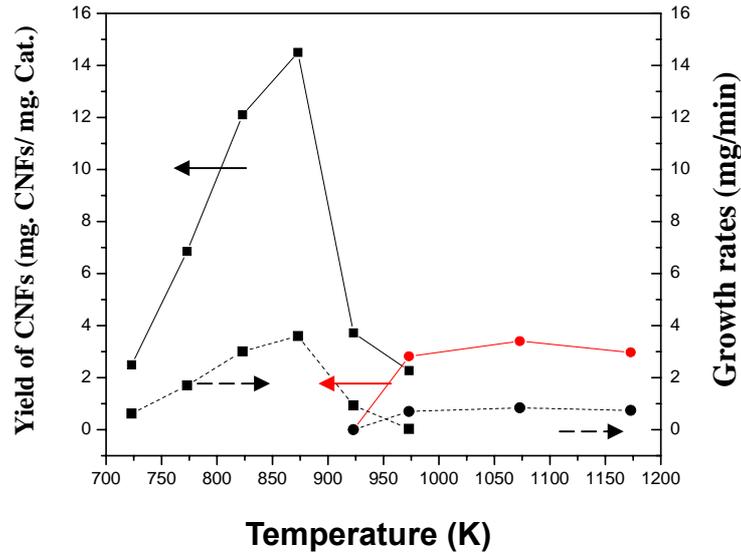


Fig. 2. Yield and growth rate of CNFs (■ : CH₄-N₂, ● : CH₄-H₂).

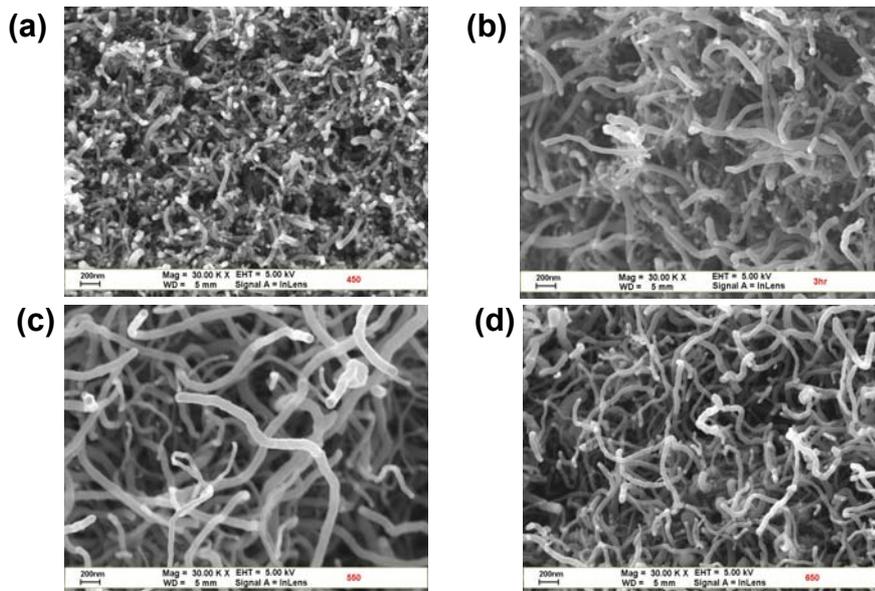


Fig. 3. CNFs deposited in CH₄-N₂ atmosphere with different temperatures: (a)723 K, (b)773 K, (c)823 K, and (d)873 K.

3.2.2 Purification of CNFs

The removal of catalyst particles in CNFs was carried out by hydrochloric acid treatment. TGA analysis as presented in Fig. 5 shows that the acid treatment will remove 85 wt.% of catalyst. After HCl or H₂O₂ purification the oxidation behavior of CNFs was modified. The oxidation temperature of CNFs was increased by about 50 K after acid treatment and was increased by about 150 K after H₂O₂ oxidation. However, the weight loss of H₂O₂ treated CNFs began at a lower temperature (~473K). TGA analysis also indicates that H₂O₂ oxidation will eliminate about 60 wt.% of the catalyst in the CNFs, which is also confirmed by the TEM observation discussed later.

However, there are still catalysts remained in the CNFs. Catalysts in CNFs can also be removed by graphitization heat treatment. TGA result (curve D) shows that the graphitization treatment can efficiently remove the catalyst.

The catalyst in this experiment is also known as an oxidation catalyst of carbon. The removal of catalyst by HCl may help to eliminate the catalyzed oxidation of CNFs and improve the oxidation resistance. As mentioned previously, H_2O_2 treatment also significantly increases the oxidation temperature. From the TEM observation (discussed later in Fig. 7) we found that the graphene layers in the CNFs are arranged at an angle with the fiber axis. The open edges of graphite plates are easily to react with foreign atoms to form functional groups. With H_2O_2 treatment these open

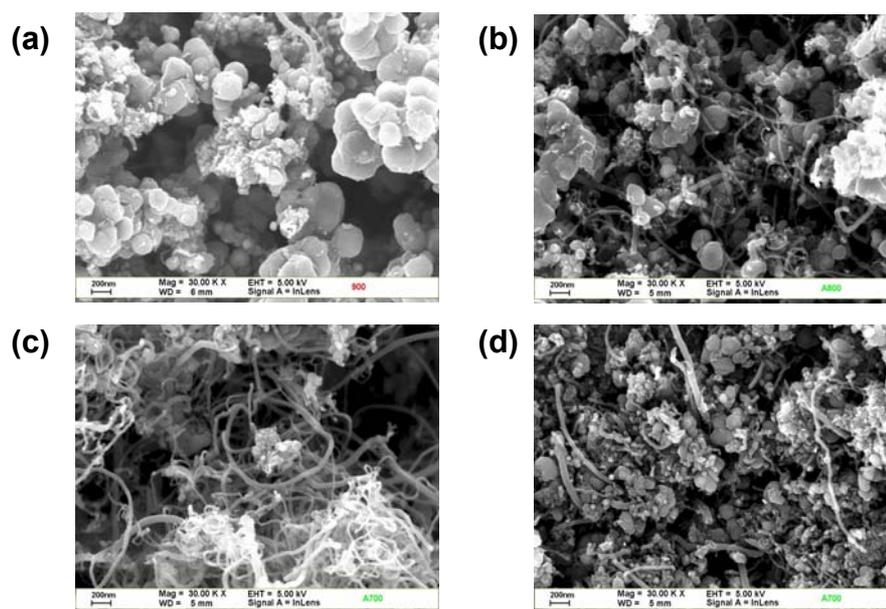


Fig. 4. CNFs deposited in CH_4-H_2 atmosphere with different temperatures: (a)1173 K, (b)1073 K, (c) and (d) 973 K.

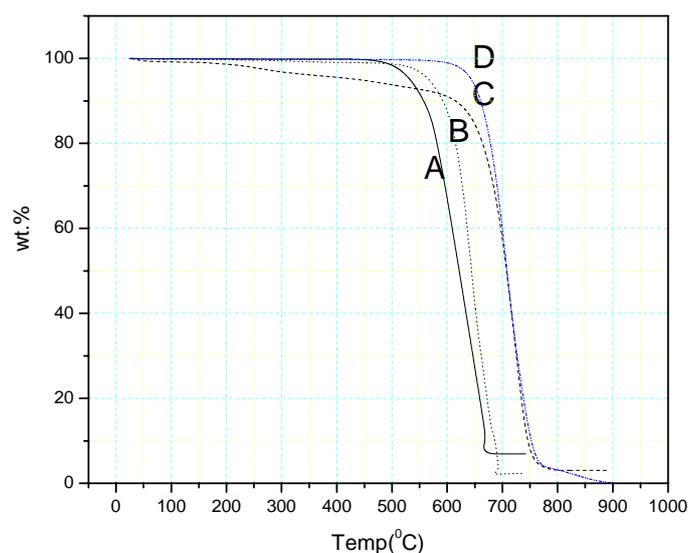


Fig. 5. The TGA curves of CNFs with different treatments (A: as-deposited at 873K, B: HCl acid washed, C: H_2O_2 oxidized, D: graphitized at 2673K).

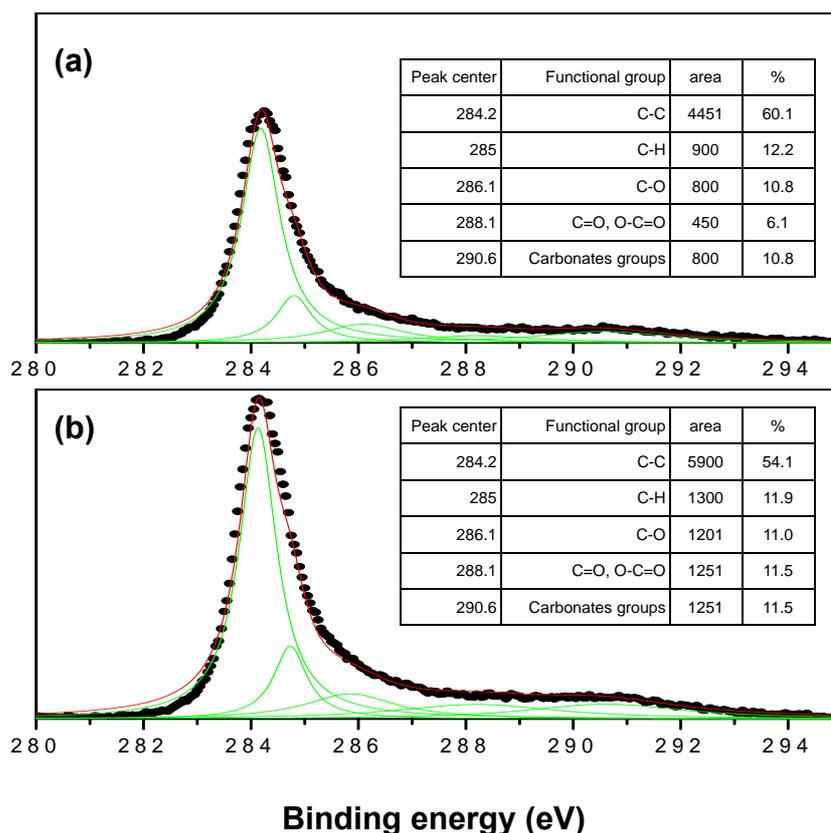


Fig. 6. ESCA spectroscopy of C1s: (a) CNFs as deposited at 873 K and (b) CNFs with H₂O₂ oxidization.

edges will easily react with oxygen. The quantitative analysis by ESCA shows that there is ~5 at.% increase of oxygen (from 1.97 to 7.09 at.%) after H₂O₂ oxidation. The further analysis of C1s scan as presented in Fig. 6 shows that the C=O and carbonate groups increase in the oxidized CNFs. The improvement of oxidation resistance by ~150 K is attributed to these oxygen-containing functional groups. However, a slight weight loss began at a lower temperature (~473K) for the oxidized CNFs.

3.3. Structure characterization of CNFs

The microstructure of CNFs was characterized by XRD and TEM as presented in Table 1 and Fig. 7. As indicated in Table 1, CNFs grown at 823K and 873K have similar d_{002} and Lc values. No obvious changes in the d_{002} and Lc values were measured after H₂O₂ oxidation. Graphitization at 2673 K increases the Lc values. However, the d_{002} value did not show obvious decrease following graphitization treatment. It is also noted that the increase in Lc value after graphitization for CNFs grown at 823 K is larger than that for CNFs grown at 873 K. Observation of TEM photographs shows that the graphite layers are arranged at an angle with the fiber axis and after graphitization the angle is smaller for CNFs grown at 873 K. Therefore, the stacking height of the graphene planes could be larger along the fiber direction for CNFs synthesized at 823 K. As discussed previously, the catalyst could also be removed after H₂O₂ oxidation treatment, which could be shown from the TEM photograph in Fig.7(d).

Table. 1 The d-spacing (d_{002}) and Lc values of as grown, graphitized, and H_2O_2 oxidized CNFs.

	Grown at 823 K	Grown at 823K and graphitized at 2673 K	Grown at 873 K	Grown at 873 K and graphitized at 2673 K	Grown at 873 K and H_2O_2 oxidized
d_{002} (Å)	3.411	3.419	3.413	3.434	3.414
Lc (Å)	127	174	121	144	111

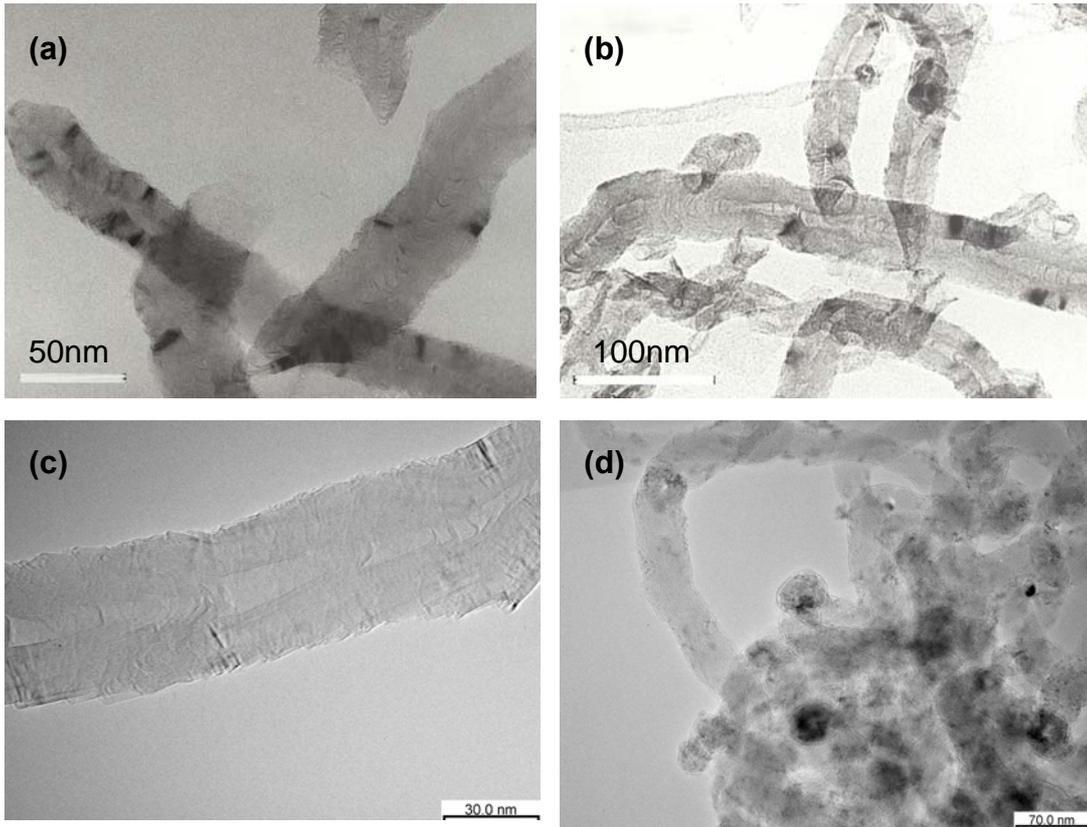


Fig. 7. TEM images of CNFs: (a) grown at 823 K and graphitized at 2673 K, (b),(c) grown at 873 K and graphitized at 2673 K, and (d) grown at 873 K and H_2O_2 oxidized.

4. Conclusions

The maximum yield of CNFs, catalytically grown using Feitknecht compound as catalyst precursor, is achieved at growth temperature of 873K when using a CH_4-N_2 atmosphere. Much less carbon yield and larger amount of non-fiber deposits were observed when using a CH_4-H_2 atmosphere. TGA analyses indicate that oxidation treatment by hydrogen peroxide can also remove the catalyst particles. The oxidation temperature of CNFs is also raised by ~ 150 K after H_2O_2 oxidation although a slight weight loss occurs at a lower temperature (~ 473 K). XRD results show that the Lc value increases slightly after graphitization at 2673 K while the d_{002} value is relatively unchanged.

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