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Article

Preparation Uniform Thin Tubular Carbon Nanofiber Using Novel Bimetallic Catalyst at Low Temperature and Its Structural Feature

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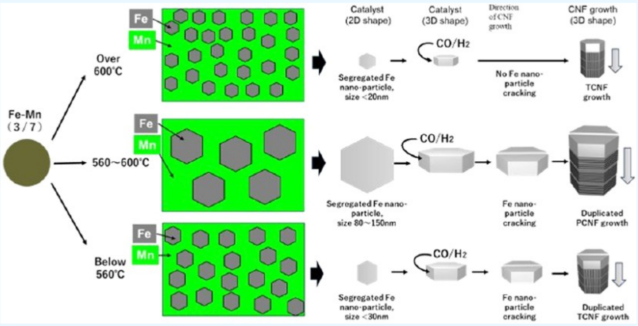
ABSTRACT: Uniform thin tubular carbon nanofibers (TCNFs), composed of two nanofibrils ca. 20 nm in diameter and with relatively high graphitic property, were prepared using a chemical deposition method from a CO/H_2 gas mix (1:4 v/v) over a novel bimetallic (Fe−Mn, 3:7 w/w) catalyst at a low temperature of 500−540 °C. Mn effectively activated the Fe catalyst when preparing selective thin TCNFs. The specific amount of Mn 70 wt % on the Fe−Mn catalyst was key for the selective preparation of uniform duplicated CNFs with an aligned tubular graphene structure. The obtained TCNFs had relatively high graphitic property; the interlayer spacing (d_{002}) and the stacking height Lc(002) were <0.3420 and >5.4 nm, respectively, because of the unique duplicated morphology.



1. INTRODUCTION

Carbon nanofiber (CNF) is a fibrous nanocarbon material with a diameter of several tens to several hundred nanometers; CNFs may assume platelet, herringbone, and tubular graphene alignments.[1−3] CNF polymer composites have found applications as conductive or flame-retarding fillers,[3−8] as catalysts in fuel cells, additives in advanced batteries and green organic synthesis platforms,[9−16] and as sensors.[17,18] Recently, CNFs have served as conductive additives combined with cathodic materials of Li-ion batteries. CNFs are an attractive alternative to carbon nanotubes (CNTs); demand for CNFs is increasing because of their unique properties and the low manufacturing cost.[19,20] Previously, CNTs were preferred to CNFs as conductive fillers, polymer composites, and the cathodic materials of Li-ion batteries because CNTs are usually smaller in diameter than CNFs and exhibit better graphene alignment (parallel to the fiber axis) than CNFs. The electrical properties of carbon materials are enhanced by their small diameter, extensive hexagonal alignment, and good graphitic properties.[19] If CNFs similar to CNTs in diameter and structure were available, they would find applications as fillers and conductive additives for composites and Li-ion batteries because of their low manufacturing costs.[21]

CNFs are usually prepared via catalytic chemical vapor deposition (CCVD) of carbon monoxide (CO) or various hydrocarbons (including methane, propane, acetylene, benzene, and ethylene) over the surface of bulk metal (Fe, Ni, or Co),[1,2] bulk metal alloy (Fe−Ni or Ni−Cu),[2,22,23] or metal-supported (Ni−Fe/carbon black or Co/MgO) catalysts[24−26] at 450−850 °C.[1,27] CNF manufacturing must be improved: CNFs must become smaller, their diameters more homogeneous, their aspect ratios (the diameter/length ratios in fiber graphitization) larger, their surface structures more controlled, and their production costs lower. In particular, there is a great need for small-diameter CNFs with tubular graphene-aligned structures such as those of CNTs. To achieve such a goal, some studies have also been conducted to manufacture tubular CNFs (TCNFs) with uniform diameter,[2] of which the applications are similar to multiwalled CNTs (MWNTs). The production temperature should be below 600 °C if CNTs are to find wide applications as effective fillers. Currently, the CNT production temperature is usually over 900 °C.[21,22]

CNF structure and diameter depend principally on both the metal catalyst employed[1,3,23,25,27] and the preparation temperature.[23] Single or bimetallic bulk Fe catalysts become very fine crystal particles under a hydrogen flow at a high temperature. CNFs become nucleated and grow over such nanocrystals when the carbon source flows.[23] Very fine (nanosized) metal particles vary in shape according to both the metal composition and the reduction temperature. In turn, these parameters define both the diameter and the hexagonal alignment of the resulting CNFs.[1,23]

We previously prepared uniform and thin tubular CNFs via CCVD of CO/H_2 over a bimetallic Fe−Ni (6:4 w/w) catalyst at 630−650 °C.[23] This catalyst yielded platelet CNFs (PCNFs)

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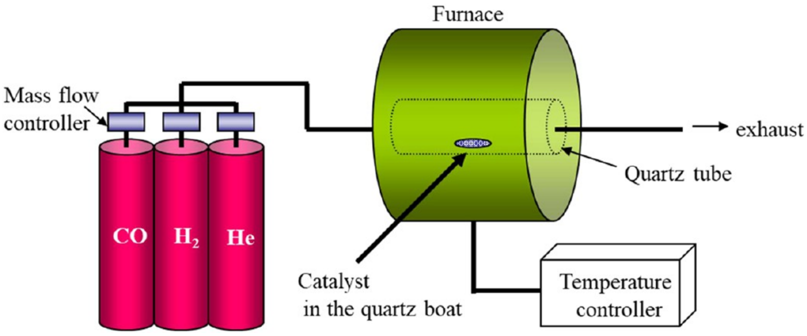


Figure 1. Schematic picture of the apparatus for the catalyst and CNF preparations.

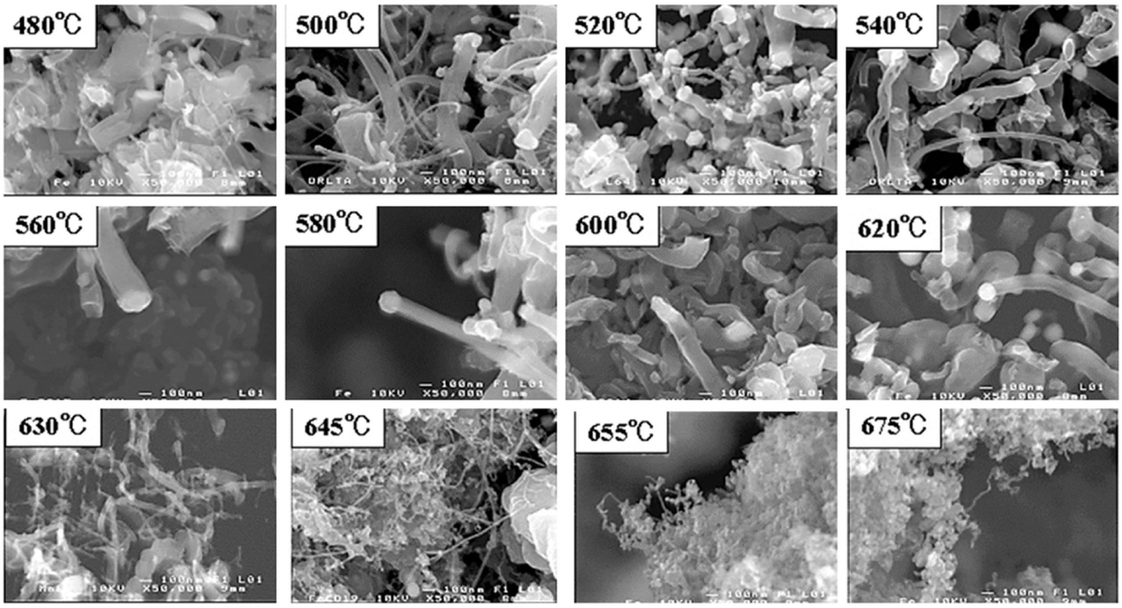


Figure 2. SEM photographs of CNFs prepared over the Fe catalyst at the temperatures of 480−675 °C.

exhibiting high graphitic property at low temperatures (below 620 °C).[23] Over 630 °C, uniform thin tubular CNFs (TCNFs) were produced. The segregated Fe particles were tens to hundreds of nanometers in size below 620 °C but suddenly decreased in size from several nanometers to tens of nanometers above 630 °C. In particular, for the Fe−Ni (6:4 w/w) catalyst, the very fine Fe was highly uniform in size (8−12 nm) compared to an Fe-only catalyst, and from the fine Fe, highly uniform thin TCNFs were successfully produced.[23]

The present study presents the fabrication of uniform thin TCNFs with high graphitization at a CCVD temperature below 550 °C. A novel bimetallic Fe−Mn catalyst was used to prepare uniform thin TCNFs at 500−675 °C using a CO/H_2 gas mixture. Fe−Mn (7:3), Fe−Mn (5:5), and Fe−Mn (3:7 w/w) catalysts were compared to an Fe-only catalyst. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the CNF diameters and graphene alignments. The graphitic properties were evaluated by X-ray diffraction (XRD). Based on the CNF morphological shapes and hexagonal alignments, the nucleation mechanism and structural features of the CNFs are discussed.

2. EXPERIMENTAL SECTION

2.1. Catalyst and CNF Preparation. CO, H_2, and Ar (99.999% pure) were purchased from Asahi Sanso Co. (Fukuoka, Japan). Reagent-grade ferric and nickel nitrates and ammonium bicarbonate were provided by Junsei Chemical (Tokyo, Japan).

Three iron−manganese (Fe−Mn) bimetallic catalysts (Fe−Mn 7:3, 5:5, and 3:7 w/w) were prepared via ammonium bicarbonate-induced precipitation of ferric and nickel carbonate from ferric and nickel nitrate solutions by the same with Fe−Ni (6:4 w/w) as described in the previous studies.[23,28,29] Fe−Mn 7:3, 5:5, and 3:7 (w/w) catalysts were prepared by the precipitation of ferric−manganese carbonates by the mechanical mixing of stoichiometrically calculated amounts of 0.5 mol of ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and manganese nitrate ($Mn(NO_3)_2{\cdot}6H_2O$) aqueous solutions using solid ammonium bicarbonate (NH_4HCO_3) for 9 h at room temperature. The obtained Fe−Mn carbonates were filtered under mild vacuum and dried at 90 °C for 4 h using atmospheric drying apparatus. The single metallic iron (Fe) only catalyst was prepared with the same method via ferric carbonate precipitation from 0.5 mol of ferric nitrate aqueous solution[28] with solid ammonium bicarbonate. The dried Fe and Fe−Mn carbonates were oxidized at 400 °C for 4 h under a flow of dry air, and then the yielded Fe and Fe−Mn oxides were reduced at 500 °C for 20 h under a H_2/Ar (1:9 v/v) flow in a conventional horizontal tube furnace. The total gas flow rate was carefully controlled to 200 mL/min (sccm)/50 mg of metal oxide. After 1 h of passivation with 5% of

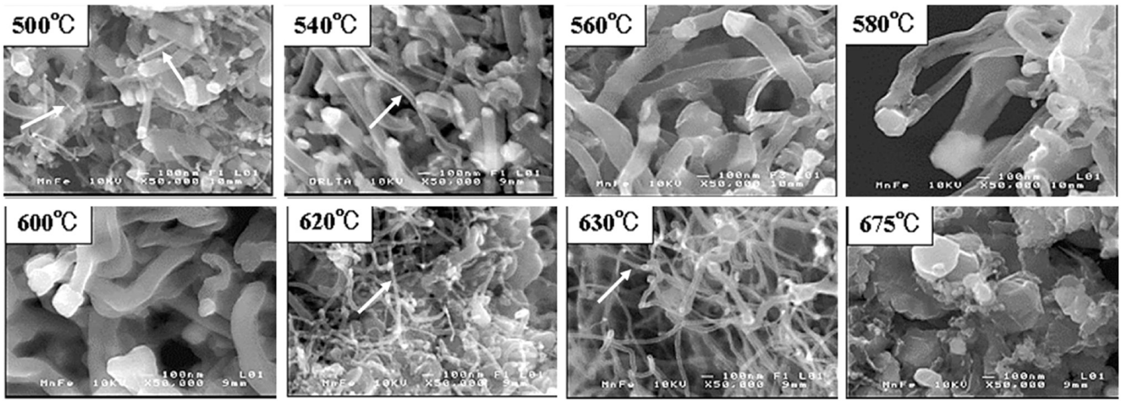


Figure 3. SEM photographs of CNFs prepared over Fe−Mn (7:3 w/w) catalyst at the temperatures of 500 −675 °C.

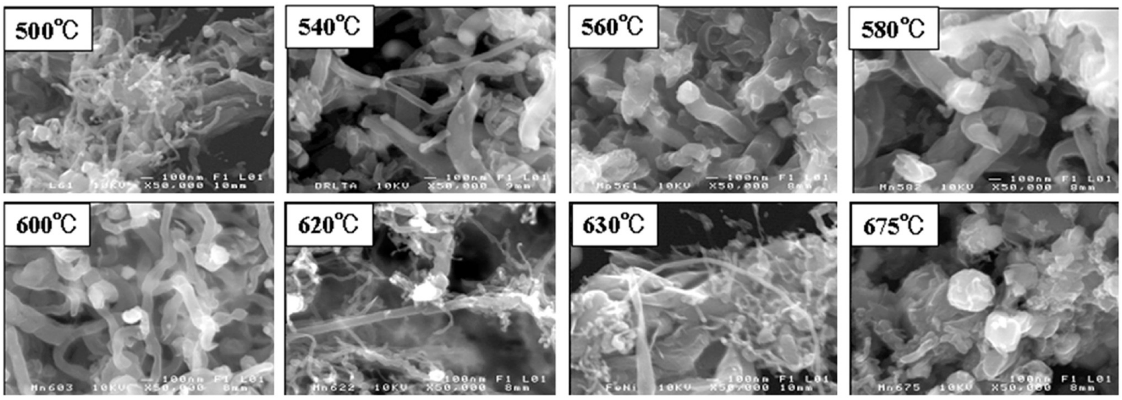


Figure 4. SEM photographs of CNFs prepared over Fe−Mn (5:5 w/w) catalyst at the temperatures of 500−675 °C.

oxygen atmosphere, Fe and Fe−Mn catalysts thus obtained were ground into particles several tens of micrometers in size and stored in an inert atmosphere.

To prepare CNFs, 30 mg amounts of ground Fe and Fe−Mn catalysts were reduced for 2 h in a H_2/Ar atmosphere at the CNF preparation temperature, and CNFs were then prepared under a CO/H_2 (1:4 v/v) flow (200 sccm) at 450−675 °C for 1 h in a conventional horizontal tube furnace with a temperature controller (Figure 1). CO/H_2 was delivered through a quartz tube (inner diameter, 41 mm; length, 500 mm). The gas flow rate was regulated by a mass flow controller (COFLOC Inc., Tokyo, Japan). The powdered Fe and Fe−Mn catalysts settled on the quartz boat at the center of the furnace quartz tube.[22,23]

2.2. Characterization. The CNF morphologies were observed by using high-resolution SEM (JEOL JSM 6700F; JEOL Co. Ltd., Tokyo, Japan) and high-resolution TEM (JEOL JEM-2010F; JEOL Co. Ltd.). Selected CNF was subjected to three dimensional (3D)-TEM using a TECNAI G2 F20 instrument (FEI Co., Yokohama, Japan). Then, two dimensional (2D)-projection images with tilt angles of −65 to +65° (2° increments, 66 images in total) were automatically acquired at 200 kV by a charge-coupled device (CCD) camera and analyzed using the inbuilt software. Then, 3D-TEM specimens were prepared via atmospheric drying of CNFs that were well-dispersed in water on TEM grids. The hourly yield of CNFs (h^{-1})is given by eq 1:

$$\text{CNF yield} = \frac{\text{weight of CNF/h} + \text{weight of catalyst}}{\text{weight of catalyst}} \qquad (1)$$

CNF graphitic properties were assessed with XRD (Rigaku Geigerflex II, Cu Kα target; Rigaku Co. Ltd., Tokyo, Japan). The graphitic parameters d_{002} and Lc(002) were calculated using the Gakushin (JSPS) method.[30]

3. RESULTS

3.1. CNFs Prepared over the Fe Catalyst. Figure 2 shows SEM photographs of CNFs prepared from CO/H_2 mixtures (1:4 v/v) over the Fe catalyst at CCVD temperatures of 480−675 °C.[31,32] At 480−540 °C, PCNFs with a larger diameter (100−300 nm) and TNCFs with a smaller diameter (20−80 nm) were mixed. At 560−620 °C, only PCNFs with 80−300 nm in diameter were apparent. At 630 °C, PCNFs and TCNFs with markedly reduced diameters (20 and 40 nm) were again mixed. Over 630 °C, only TCNFs with 20−80 nm in diameter were evident. The extent of graphene alignment was thus affected by temperature, as reported previously.[22,23] However, TCNF formation below 540 °C was not found in the previous study because we did not carry out the CNF production below 540 °C. Also, TCNFs prepared below 540 °C appeared thinner and more linear compared to TCNFs prepared above 630 °C.

3.2. CNFs Produced over Fe−Mn Catalysts. Figures 3−5 show SEM photographs of CNFs prepared from CO/H_2 mixtures (1:4 vo/vol) over Fe−Mn (7:3 w/w), Mn (5:5 w/w), and Mn (3:7 w/w) catalysts at 500−675 °C.

In Figure 3, at 500−540 °C, CNFs prepared over Fe/Mn (7:3 w/w) included graphene-aligned PCNFs 80−300 nm in diameter and TCNFs 15−30 nm in diameter, similar to those produced using Fe alone as the catalyst. At 560−600 °C, only PCNFs 80−300 nm in diameter were apparent. At 620−640 °C,

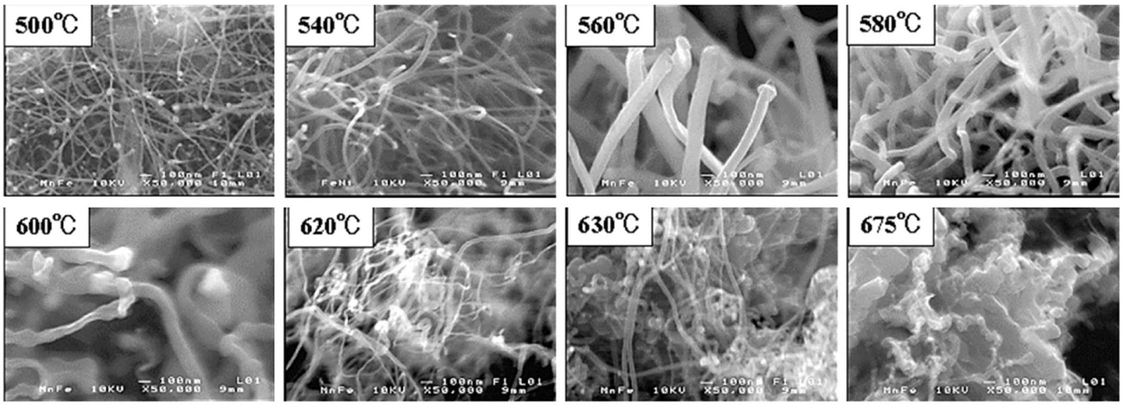


Figure 5. SEM photographs of CNFs prepared over Fe−Mn (3:7 w/w) catalyst at the temperatures of 500−675 °C.

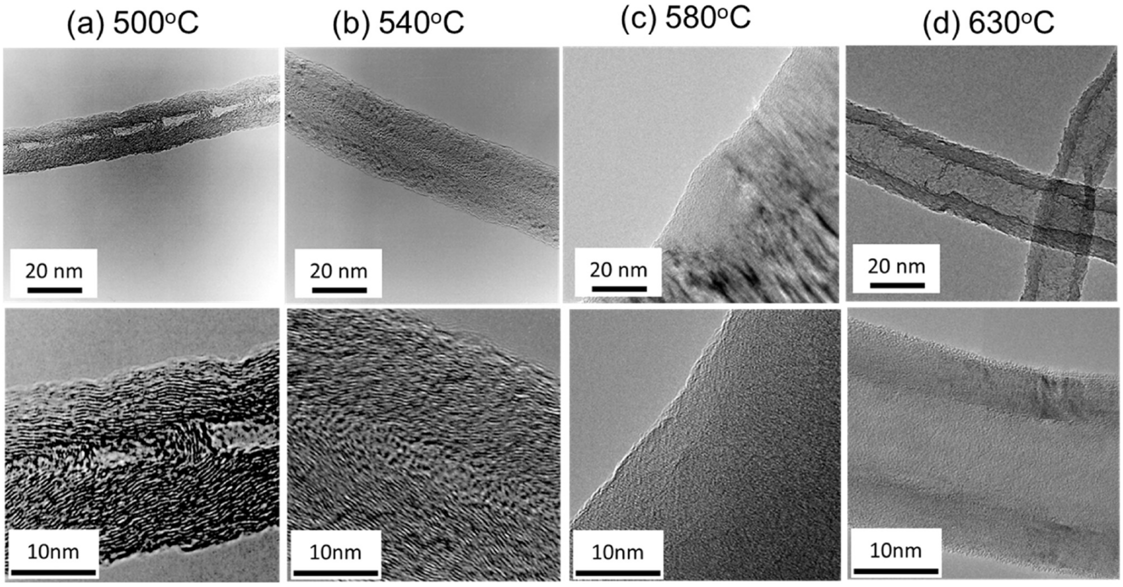


Figure 6. TEM images of CNFs prepared over Fe−Mn (3:7 w/w) catalyst at (a) 500 °C, (b) 540 °C, (c) 580 °C, and (d) 630 °C.

PCNFs 100−300 nm in diameter and TCNFs 20−40 nm in diameter were again mixed. At 675 °C, only a few TCNFs appeared. Notably, the highest temperature at which TCNFs formed and grew fell from 630 °C for the Fe-only catalyst to 620 °C for the Fe−Mn (3:7 w/w) catalyst, and the latter TCNFs were more uniform and linear. Few CNFs were evident at 675 °C. The changes may indicate alloying effects when Mn is added to Fe.

Figure 4 shows SEM photographs of CNFs prepared from the CO/H_2 mixture over the Fe−Mn (5:5 w/w) catalyst at 500−675 °C. The CNFs were similar to those prepared over the Fe−Mn (7:3 w/w) catalyst, but the alloying effect of Mn was greater. At 500−540 °C, the CNFs prepared over Fe/Mn (5:5 w/w) exhibited graphene-aligned PCNFs 80−300 nm in diameter and TCNFs 15−40 nm in diameter. At 560−600 °C, only PCNFs 80−300 nm in diameter were apparent. At 620−640 °C, PCNFs 100−300 nm in diameter and TCNFs 15−40 nm in diameter were again mixed. At 675 °C, there were few CNFs.

Figure 5 shows SEM images of CNFs produced from the CO/H_2 mixture over the Fe−Mn (3:7 w/w) catalyst at 500−675 °C. Below 600 °C, the CNF diameter was much more uniform than that described above; Mn/Fe alloying was then optimized. At 500−540 °C, only uniform TCNFs 15−40 nm in diameter were apparent. TCNFs prepared at 500 °C were very uniform, thin (diameter 15−25 nm, ca. 20 nm), and linear. At 560−600 °C, only PCNFs 80−300 nm in diameter were evident. PCNFs prepared at 560 °C were very uniform and linear. At 620−640 °C, TCNFs 15−40 nm in diameter and some carbon-coated catalyst coagulate were mixed. At 675 °C, only a few TCNFs were evident.

3.3. TEM of CNFs Prepared over Fe−Mn (3:7 w/w).

Figure 6 shows TEM images of CNFs prepared over the Fe−Mn (3:7) catalyst at 500, 540, 580, and 630 °C. CNFs prepared at 630 °C exhibited a well-developed, tubular-type graphene alignment. The CNFs prepared at 580 °C were typical PCNFs. CNFs prepared at 540 °C exhibited a tubular-type graphene alignment with some degree of core herringbone structure. CNFs prepared at 500 °C exhibited tubular-type graphene alignment with some core ladder-like bridges. The TCNFs prepared at 540 and 630 °C differed in terms of the internal tube diameter and wall thickness. TCNFs prepared at 630 °C had larger internal tubes (10−15 nm in diameter); the tube diameters of those prepared at 500 and 540 °C were <6 nm.

3.4. CNF Yields and Structures.

Figure 7 shows the CNF yields in the first hour over the Fe and Fe−Mn catalysts. Table 1 summarizes the yields and structures. The Fe-only catalyst always exhibited the highest CNF yields. Of the Fe−Mn catalysts, Fe−Mn (7:3) and Fe−Mn (5:5 w/w) had similar CNF

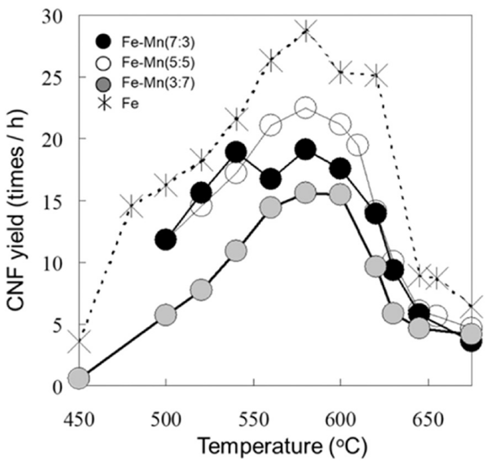


Figure 7. CNF yields prepared over the Fe and Fe−Mn bimetallic catalysts.

yields, and Fe−Mn (3:7 w/w) had lower yields. In detail, the Fe−Mn (7:3 w/w) yield was slightly lower than that of Fe−Mn (5:5 w/w) at 560−600 °C when PCNFs formed. The PCNF yield was much higher than that of TCNF (Table 1). For the Fe−Mn (3:7 w/w) catalyst, the TCNF yields at 500 °C−540 °C were 5.6−10.5 (times/h), but the PCNF yields at 560 °C−600 °C were higher by 14.0−15.2% (times/h) when only PCNFs formed.

Figure 8 phenomenologically explains the changes of the Fe−Mn (3:7 w/w) catalyst and the growth of CNFs from CO/H_2 (1:4 v/v) according to temperatures. Fe nanoparticles were segregated from the Fe−Mn (3:7 w/w) catalyst to sizes less than 20 nm at temperatures above 600 °C, 80−150 nm at temperatures 560 °C−600 °C, and less than 30 nm at temperatures below 560 °C. Relatively homogeneous tubular CNFs (TCNFs) were grown from the segregated Fe nanoparticles less than 20 nm generated at temperatures above 600 °C without cracking of Fe nanoparticles at over 600 °C under a CO/H_2 flow atmosphere. Duplicated platelet CNFs (PCNFs) were grown from the segregated Fe nanoparticles of 80−150 nm generated at temperatures 540−600 °C due to cracking of Fe nanoparticles at the early stage of CNF growth at temperatures 540−600 °C under a CO/H_2 flow atmosphere. Uniform and homogeneous duplicated tubular CNFs (TCNFs) were grown from the segregated Fe nanoparticles of less than 30 nm produced at a temperature below 540 °C due to cracking of the Fe nanoparticles at the early stage of CNF growth under a CO/H_2 flow atmosphere. Here, it is still not clear why the segregated Fe fine particles crack into two pentagonal shaped particles at the early stage of CNF formation at temperatures below 600 °C. We believe that the reason for cracking and its driving force for cracking need to be clarified in the future. PCNFs and TCNFs could be selectively prepared by controlling the temperature. The yields at 500, 520, 540, 620, 630, and 645 °C (TCNFs only) were 5.6, 7.4, 10.5, 8.0, 5.8, and 4.8/h, respectively, lower than those at 560, 580, and 600 °C (PCNFs only; 14.0, 15.2, and 15.1/h, respectively). The reason for this may be (as suggested previously)[23] that a smaller catalyst associated with TCNF formation is less active than a larger catalyst yielding PCNFs.

3.5. Graphitic Properties of CNFs Prepared over Fe−Mn Catalysts.

Figure 9 shows the interlayer spacing (d_{002}) and stacking height (Lc(002)) of CNFs prepared over the Fe and Fe−Mn catalysts; the calculations were performed using the JSPS method.[30] All CNFs were higher graphitic than usual CNTs, and all d_{002} and Lc(002) values were below 0.3420 nm and above 5.8 nm, respectively.[20] CNFs prepared over Fe, Fe−Mn (7:3 w/w), and Fe−Mn (5:5 w/w) were similar in terms of both parameters; CNFs produced over Fe−Mn (3:7 w/w) exhibited relatively larger d_{002} values and relatively smaller Lc(002) values. The d_{002} value of TCNFs prepared over Fe−Mn (3:7 w/w) at 500 °C was 0.3420 nm but decreased to 0.3390 nm at 540 °C; the minimum PCNF value (0.3356 nm) occurred at 600 °C, and it then increased once more to 0.3372 nm for TCNFs formed at 645 °C. The TCNF interlayer spacings were larger than those of PCNFs [Figure 9a]. Of all of the TCNFs, those prepared at lower temperatures (500−540 °C) exhibited larger interlayer spacings than those prepared at higher temperatures (620−675 °C).

The Lc(002) values of TCNFs prepared over Fe−Mn (3:7 w/w) were 5.8−6.2 nm at 500−540 °C, increased to 8.5 nm at 540 °C, peaked at 12.8 nm in PCNFs prepared at 600 °C, and then decreased to 10.3, 9.8, 10.2, and 10.5 nm in TCNFs prepared at 620, 630, 645, and 675 °C, respectively. Figure 9b shows that the stacking heights of TCNFs were smaller than those of PCNFs.

4. DISCUSSION

4.1. Structural Features of TCNFs Prepared over Fe−Mn (3:7 w/w).

We first confirmed that the bulk Fe−Mn (3:7 w/w) bimetallic catalyst became homogeneously segregated into highly uniform nanosized grains below 550 °C under H_2 and that such grains allowed the CO source gas to nucleate and grow uniform TCNFs with relatively high linearity. In particular, TCNFs prepared over Fe−Mn (3:7 w/w) at 500−540 °C exhibited relatively good graphitic properties, including lower interlayer spacings and greater stacking heights than traditional CNTs. We next used TEM to examine the CNF structures. Figure 10 shows TEM images of CNFs prepared over Fe−Mn

Table 1. Yields and Structures of CNFs Prepared over Fe and Fe−Mn Bimetallic Catalysts

catalyst		preparation temperature (°C)											
		450	480	500	520	540	560	580	600	620	630	645	675
Fe	CNF yield[a]	3.8	14.6	15.8	17.0	21.0	26.1	28.3	25.1	25.0		7.4	6.0
	structure	P + T	P + T	P + T	P + T	P + T	P[b]	P	P	P	P + T	T[c]	T
Fe−Mn (7:3 w/w)	CNF yield			12.0	15.2	18.2	16.0	18.0	17.0	13.6	8.7	5.4	4.6
	structure			P + T		P + T	P	P	P	P + T	T		T
Fe−Mn (5:5 w/w)	CNF yield			12.1	14.3	16.4	20.5	21.8	20.4	13.8	9.2	5.5	4.8
	structure			P + T		P + T	P	P	P	P + T	P + T		T
Fe−Mn (3:7 w/w)	CNF yield	2.1		5.6	7.4	10.5	14.0	15.2	15.1	8.0	5.8	4.8	4.7
	structure			T	T	T	P	P	P	T	T		T

[a] CNF yield (times/h) = (Weight of CNF(/h) + Weight of catalyst)/(Weight of catalyst). [b] P: platelet CNF. [c] T: tubular CNF.

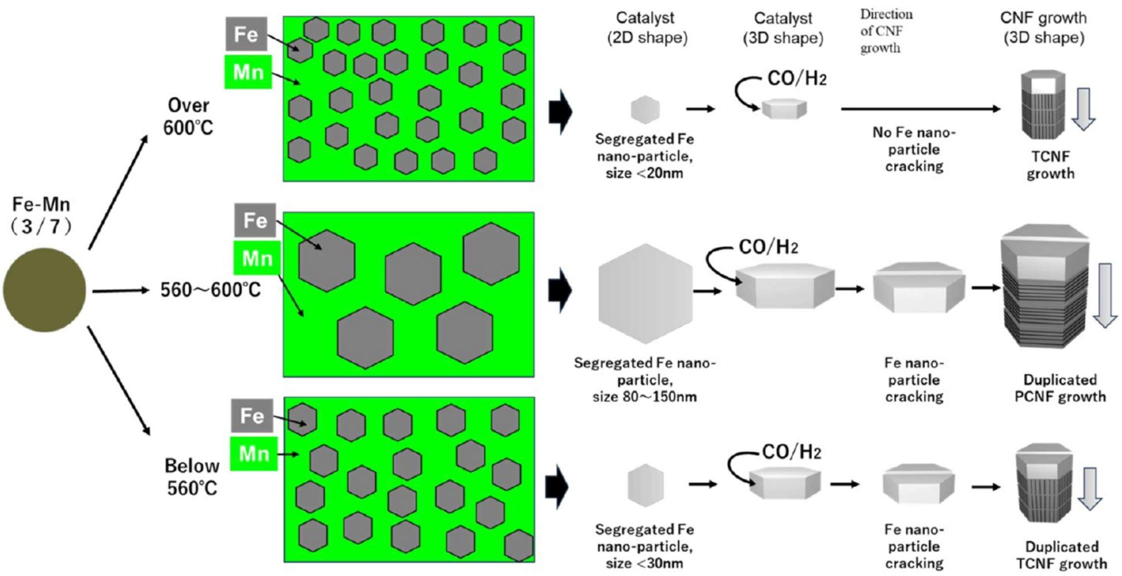
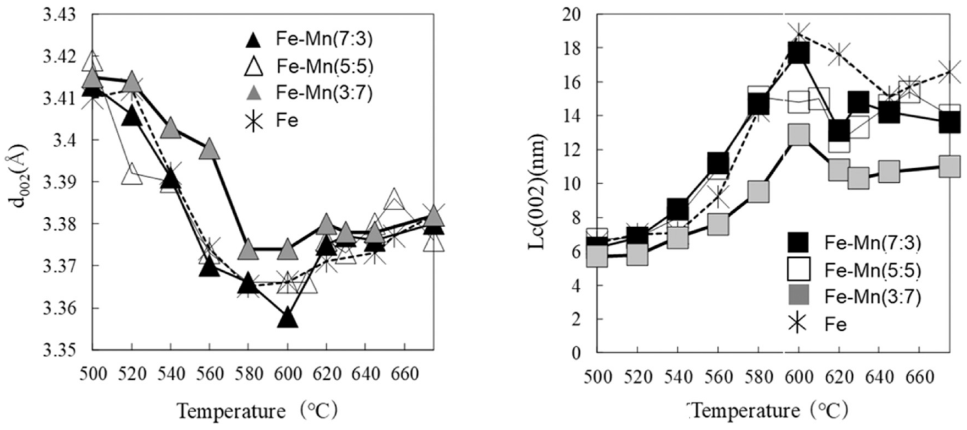


Figure 8. Phenomenological changes of the Fe−Mn (3:7 w/w) catalyst and the growth of its derived CNFs under the CO/H_2 flow atmosphere according to the preparation temperatures.



(a) Interlayer spacing (b) Stacking height

Figure 9. Graphitic property of CNFs prepared over Fe and Fe−Mn bimetallic catalysts: (a) interlayer spacing (d_{002}) and (b) stacking height (Lc(002)).

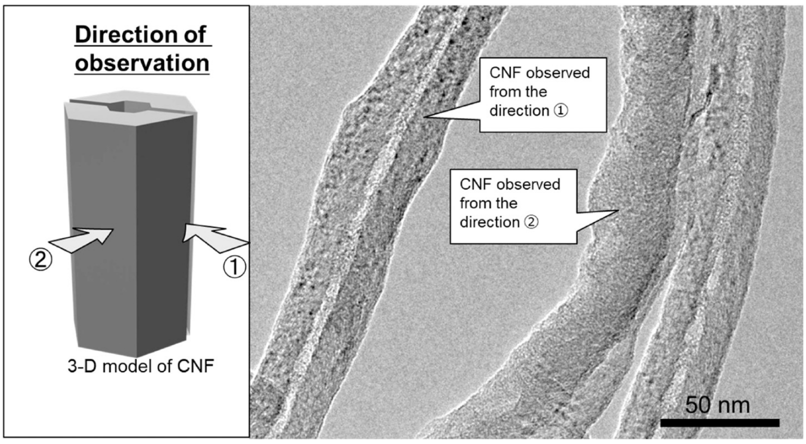


Figure 10. TEM image of TCNF prepared over the Fe−Mn (3:7 w/w) catalyst at 540 °C.

(3:7 w/w) at 540 °C. Unlike the TCNFs shown in Figures 6 and 8, Figure 10 shows TCNFs of two different morphological images by the direction of observation: with and without continuous internal tubes. These different morphological images of TCNF reflect the duplication of two separate nanofibrils. More specifically, two nanofibrils with tubular graphene-type

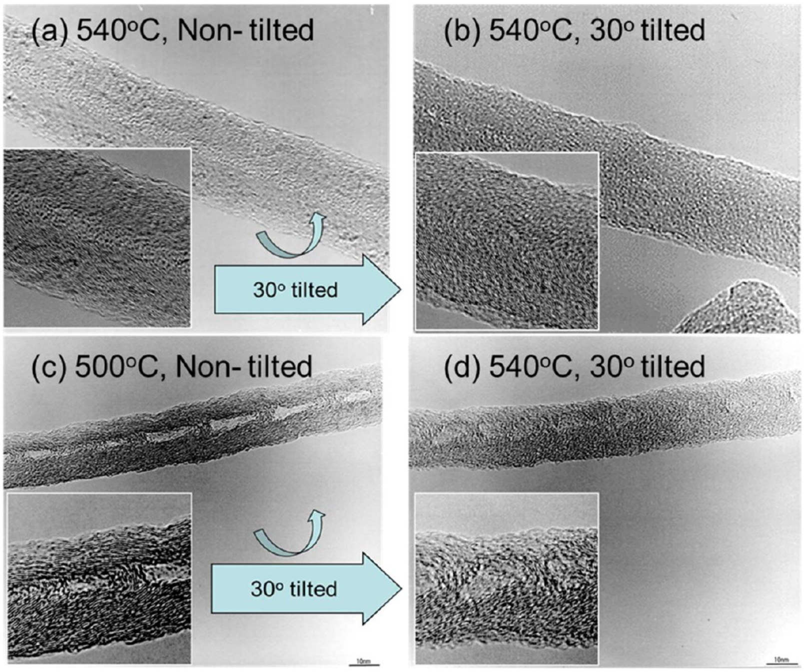


Figure 11. Nontilted and 30° tilted TEM images of TCNFs prepared over Fe−Mn (3:7 w/w) catalyst at (a, b) 540 °C and (c, d) 500 °C.

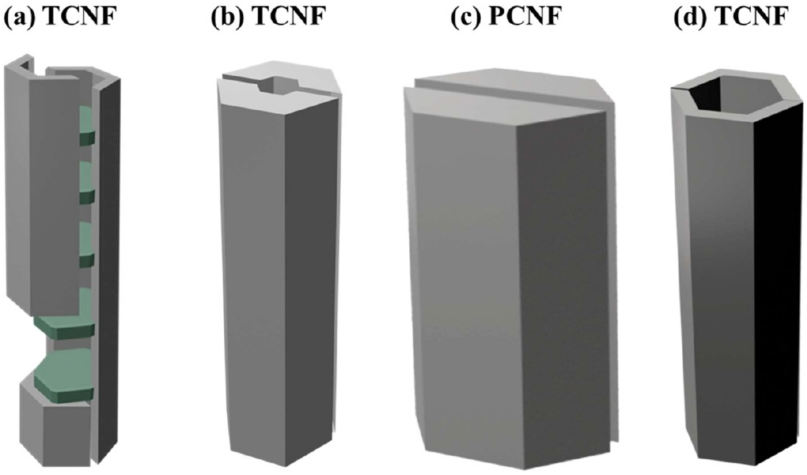


Figure 12. Schematic 3D models of CNFs prepared over the Fe−Mn (3:7 w/w) catalyst at (a) 500 °C and (b) 520−540 °C, (c) 560−600 °C, and (d) over 620 °C.

aligned structures combined to form a single TCNF, the morphology of which differed by the direction of observation (arrows ① and ② in Figure 10). Figure 11 shows TEM images of TCNFs prepared over Fe−Mn (3:7 w/w) at 500 and 540 °C but now tilted by 0 and 30°. In TCNFs prepared at 540 °C, it is difficult to observe the internal tubes after tilting through 30° [Figure 11a,b]. TCNFs at 500−540 °C exhibited some periodical ladder-type bridges in the internal tubes; these were clearly apparent after tilting [Figure 11c,d]. Thus, TCNFs prepared over the Fe−Mn (3:7 w/w) catalyst at 500−540 °C had two duplicated nanofibrils connected by periodic ladder-type bridges. An attempt was made to view TCNFs prepared at 540 °C, but the resolution was poor. The 3D images clearly show that the PCNFs also had twin nanofibrils of platelet-type graphene. TCNFs prepared at 500−540 °C and PCNFs prepared at 560−600 °C both had unique twinned nanofibrils. The catalyst was hexagonal in 2D [Figure S1(a)]; the PCNFs and TCNFs exhibited hexagonal cross sections because both twin nanofibrils had pentagonal cross sections. It remains unclear how the duplicated CNFs formed. During CNF nucleation, it may be that an unknown shear force breaks the catalyst into two pieces; more work is required to confirm this.

4.2. Morphologies of CNFs Prepared over the Fe−Mn (3:7 w/w) Catalyst.

Figure 12 shows the proposed morphologies of CNFs prepared over the Fe−Mn (3:7 w/w) catalyst. The models explain why TCNFs prepared at 500−540 °C are more graphitic than CNTs. These TCNFs exhibit hexagonal cross sections, attributable to the twin nanofibrils with pentagonal cross sections. The curvature of the CNF cross section that shows graphene stacking was flatter (less bent) than that of the typical round-shaped CNT cross section, which must be one of the reasons that the obtained TCNFs showed relatively high graphitic properties than those of usual CNTs. CNFs prepared over the Fe−Mn (3:7 w/w) catalyst at 500−540 °C may serve as highly effective catalysts because their internal

Table 2. Preparation Condition and Some Physical Properties of Various TCNFs and MWNT

						physical properties		
	preparation condition and maximum yield[a]						graphitic property	
sample	catalyst	T (°C)	gas	yield (wt %)	surface area[b] (m^2/g)	shape and diameter of transversal section (nm)	d_{002} (nm)	Lc(002) (nm)
duplicated TCNF	Fe−Mn (3:7 w/w)	540	CO/H_2 (1:1 v/v)	18−24	84	hexagonal (duplicated) avg. 28	0.351	6.42
TCNF[23,c]	Fe−Ni (6:4 w/w)	630	CO/H_2 (4:1 v/v)	12	54	hexagonal avg. 20	0.337	4.40
TCNF[24,c]	Co/MgO (3:7 w/w)	600	C_2H_4/H_2 (4:1 v/v)	24	50	round avg. 22	0.352	2.71
MWCNT[33,c]		>900	CH_4/H_2 (?)		67	round avg. 15	0.362	1.71

[a] Maximum yield was evaluated by (The weight of (CNF + catalyst)/The weight of catalyst after 5 h of preparation). [b] Specific surface area was measured and calculated by the N_2−BET method. [c] Reference No.

surfaces (i.e., not only their external surfaces) may be catalytically active.

The characteristic physical properties of the newly prepared duplicated TCNF at a temperature of 540 °C are summarized in Table 2 in comparison with other TCNFs[23,24] and MWNT.[33] It was confirmed that the duplicated TCNF exhibited a relatively high specific surface area and a high degree of graphitization, despite being prepared at a low temperature.

5. CONCLUSIONS

Uniform thin TCNFs with twin nanofibrils ca. 20 nm in diameter and relatively good graphitic properties were prepared via chemical deposition from CO/H_2 (1:4 v/v) over a novel bimetallic catalyst [Fe−Mn 3:7 w/w] at low temperature (500−540 °C):

1. In the bimetallic catalyst of Fe−Mn, the Mn proportion on the Fe−Mn catalyst was key for the selective preparation of tubular and plate-type aligned graphene structures; the obtained CNFs over Fe−Mn (3:7 wt./wt) were uniform in morphology without showing the mixed morphologies of PCNF and TCNF.
2. The CNFs prepared over Fe−Mn (3:7 w/w) at the temperature range 560−600 °C were typical PCNFs. CNFs prepared at the temperature range 500−540 °C exhibited a tubular-type graphene alignment with some degree of core herringbone structure. CNFs prepared at 500 °C especially exhibited tubular-type graphene alignment with some core ladder-like bridges. The TCNFs prepared at 540 and 630 °C differed in terms of the internal tube diameter and wall thickness. TCNFs prepared at 630 °C had larger internal tubes (10−15 nm in diameter); the tube diameters of those prepared at 500 and 540 °C were <6 nm.
3. The Fe-only catalyst always exhibited the highest CNF yields. Of the Fe−Mn catalysts, Fe−Mn (7:3) and Fe−Mn (5:5 w/w) had similar CNF yields, and Fe−Mn (3:7 w/w) had lower yields. In detail, the Fe−Mn (7:3 w/w) yield was slightly lower than that of Fe−Mn (5:5 w/w) at 560−600 °C when PCNFs formed. The PCNF yield was much higher than that of TCNF. For the Fe−Mn (3:7 w/w) catalyst, the TCNF yields at 500 °C−540 °C were 5.6−10.5 (times/h) but the PCNF yields at 560 °C−600 °C were higher by 14.0−15.2 (times/h) when only PCNFs formed.
4. The TCNFs prepared over Fe−Mn (3:7 w/w) below 550 °C had high graphitic property; the interlayer spacing (d_{002}) and the stacking height Lc(002) were <0.3401 nm and >5.4 nm, respectively. The TCNFs exhibit a unique structure and morphology.
5. From TEM observations, the CNFs prepared over Fe−Mn (3:7 w/w) at 500, 540, and 580 °C showed particular morphologies of PCNF and TCNF of reflecting the duplication of two separate nanofibrils. More specifically, two nanofibrils with tubular and platelet graphene-type aligned structures combined to form a single TCNF and PCNF, respectively. The TCNF prepared over the Fe−Mn (3:7 w/w) catalyst at 500 °C had two duplicated nanofibrils connected by periodic ladder-type bridges.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c10295.

3D-TEM observation of Fe Mn-catalyzed CNF growth; in addition, TEM observations are being made at various temperatures (PDF)

3D-TEM image of FM37 600 (AVI)

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Notes

The authors declare no competing financial interest.

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