



The morphology, porosity and productivity control of carbon nanofibers or nanotubes on modified activated carbon

Xiao-Wei Chen^a, Dang Sheng Su^{a,*}, Sharifah B.A. Hamid^b and Robert Schlögl^a

^aFritz-Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany

^bCombinatorial Technology and Catalysis Research Center, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding author. Tel.: +49 30 84135406; fax: +49 30 84134401; email: dangsheng@fhi-berlin.mpg.de

Since their discovery, carbon nanotubes and carbon nanofibers (CNTs or CNFs) have exhibited potential in a wide range of physical and chemical applications [1] and [2]. For applications in gas phase catalysis, loose CNTs or CNFs are unsuited because they limit the catalyst–reactant transport properties and they are difficult to handle when filling in the reactor tubes. In addition, there is a health risk associated with loose CNTs or CNFs [3]. Immobilizing CNTs or CNFs on a supporting material is thus highly desirable. CNFs or CNTs have previously been grown on carbon materials, particularly on CNT or CNF support [4], [5], [6] and [7]. Activated carbon (AC) has been widely used as an efficient adsorbent for the purification of water, air and many fluid synthetic and natural products [8]. Previously we have reported that CNFs nested inside and immobilized onto modified AC exhibit an excellent adsorption behavior for heteropolymolybdate compared to metal cations [9]. The productivity of CNFs and CNTs is a function of the preparation conditions, such as nature of the substrate and of the catalyst, temperature, gas composition and time on stream [10] and [11]. In this work, a systematic study was conducted of the parameters for the synthesis of CNFs from C₂H₄ on modified AC. The productivity, porosity and morphology of the CNF/AC composites can be controlled with iron salt precursors, the ratio of C₂H₄/H₂, the reaction temperature and the reaction time.

The preparation procedures of Fe/AC catalysts and CNF/AC composites have been described in our previous work [9]. Before impregnation, the AC was calcined at 400 °C for 4 h in air. The pH values of iron nitrate, iron acetate and iron citrate aqueous solutions were adjusted to 2.0 with NH₃·H₂O aqueous solution or concentrated acetic acid respectively. The 1 wt% Fe/AC catalysts were prepared by incipient wetness impregnation using 0.09 M aqueous solutions of iron citrate, iron acetate and iron nitrate (2.0 cm³) and modified AC (1 g). During the CNF or CNT growth, the temperature was varied between 500 and 800 °C, while reaction time was varied from 10 to 120 min.

The elemental analysis shows that the carbon, hydrogen, nitrogen and oxygen in the raw AC are 92.42, 0.46, 0.35 and 0.82 wt%. The total content of Fe and Ca is about 2.91%. The rest components are silicon, potassium, and other impurities. A blank experiment was also performed on the modified AC. After reaction of a mixture of ethylene and H₂ at 700 °C for 2 h, the weight of AC increases from 100 to 130 mg indicating that carbon deposits on the AC. Scanning electron microscopy (SEM) confirms that carbon is deposited in the form of CNFs with diameters in the range from 20 to 500 nm.

The iron particles prepared with iron nitrate are the largest with the particle size distribution from 20 to 200 nm. The average size of iron particles obtained using iron acetate is about 20 nm. Iron particles are not readily found when using iron citrate as precursor. However, iron can be detected by energy dispersive X-ray analysis, indicating that iron is well-dispersed on the surface of the AC. The difference in iron particle sizes of the Fe/AC catalysts leads to different diameters of CNFs on AC. The order of CNF diameters prepared with different iron precursors is: iron

nitrate > iron acetate > iron citrate (Fig. 1). Similar to our previous work [9], CNFs can be observed not only on the surface but also in the pores of AC.

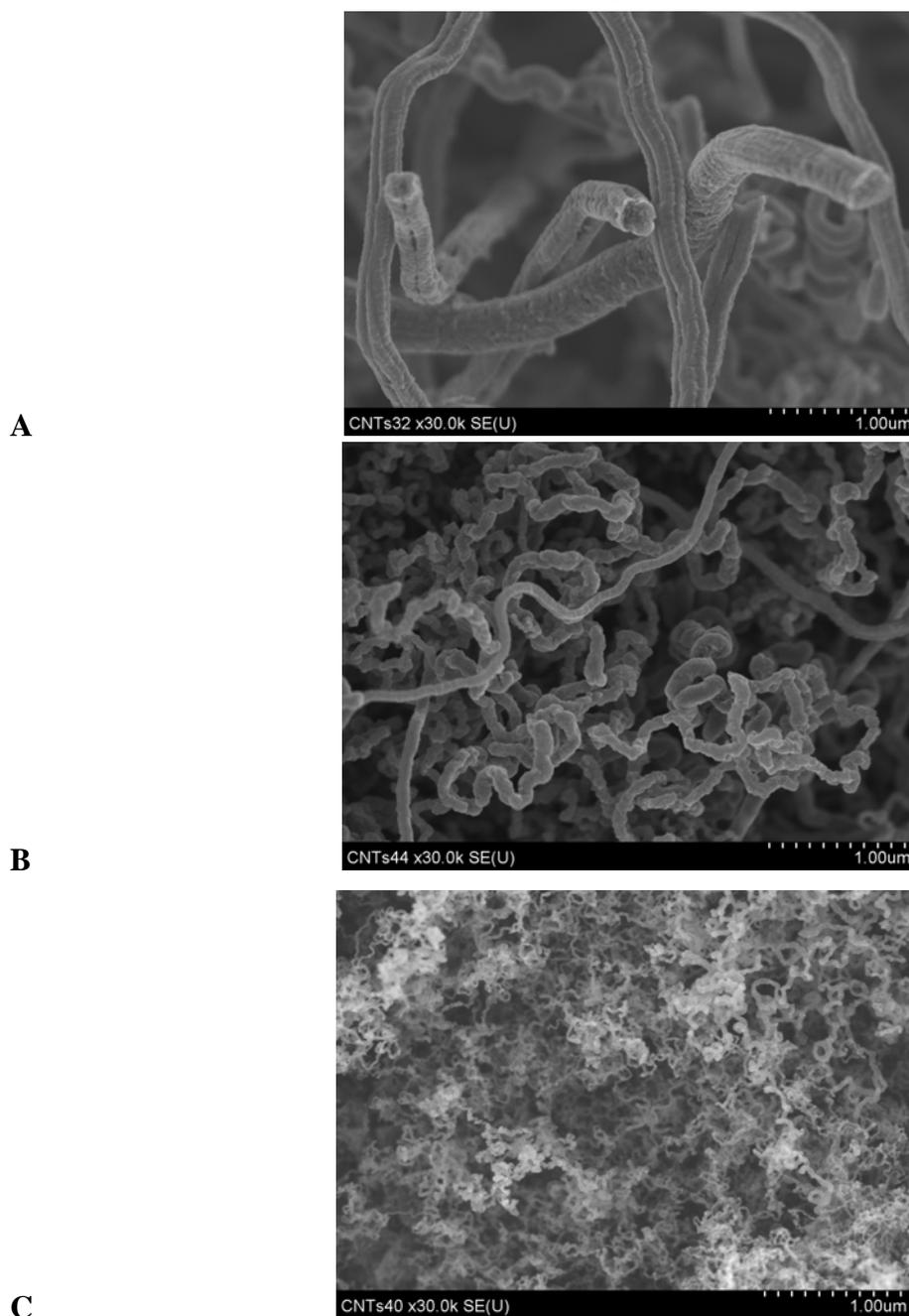


Figure 1. CNF/AC composites prepared with different iron precursors: (A) iron nitrate, (B) iron acetate and (C) iron citrate. Scale bar: 1 μm .

Table 1 summarizes the productivities, BET surface areas, pore volumes and diameter distributions of CNF/AC composites as a function of iron precursors. The Fe/AC catalyst prepared with iron nitrate gives the highest productivity of CNFs on AC (107.6 g C/g Fe), whereas the productivity of catalysts prepared with iron citrate and iron acetate is 62.5 and 53.3 g C/g Fe, respectively. The BET specific surface areas of the CNF/AC composites decrease from 1237 to less than 100 m^2/g . Meanwhile, the total pore volume decreases from 0.547 to around 0.08 cm^3/g . The dramatic decreases of BET specific surface area and pore volume for CNF/AC composites are attributed to the decrease of micropores of CNF/AC composites. The Fe/AC catalyst prepared with iron nitrate produces the biggest diameters of CNFs and the highest productivity of CNFs on AC. In the following experiments, iron nitrate was chosen as the iron precursor.

Table 1 Productivities, BET surface areas, pore volumes and diameter distributions of CNF/AC composites as a function of iron precursor. Synthesis conditions: 1 wt% Fe/AC catalyst, C₂H₄:H₂ = 50:50 cm³/min, 700 °C for 2 h.

Samples	Fe precursor	Productivity (g C/g Fe)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Diameter distribution	
						Diameter range (nm)	Dominant diameter (nm)
AC			1081	0.365	-		
AC-400			1237	0.547	0.514		
CNTs-40	Fe citrate	62.5	17.7	0.009	0.029	20-100	20
CNTs-44	Fe acetate	53.3	91.5	0.078	0.048	50-200	100
CNTs-32	Fe nitrate	107.6	56.0	0.080	0.038	50-400	200

The ratio of hydrocarbon to hydrogen is essential for the CNT or CNF growth [10] and [11]. H₂ might have an impact on both the morphology and productivity of CNTs or CNFs. The total flow rate of the C₂H₄ and H₂ mixture is 100 cm³/min. When only H₂ was introduced into the Fe/AC catalyst bed, no CNFs were produced and only Fe particle was observed. When the ratio of C₂H₄ to H₂ was 2:8, CNFs were observed on the surface of the Fe/AC catalyst. The diameters of most CNFs were between 150 to 1000 nm. The diameters of CNFs are more uniform and less than 300 nm when the C₂H₄:H₂ ratio is 5:5. The diameters of CNFs become smaller with increasing C₂H₄/H₂ ratio. The diameters of CNFs prepared with pure C₂H₄ are less than 100 nm. HRTEM images confirm that graphite layer of a CNT formed when only C₂H₄ was introduced into the Fe/AC catalyst bed. The productivities of CNFs are 0, 70, 107.6, 62.5 and 53 g C/g Fe when the C₂H₄/H₂ ratios are 0:1, 2:8, 5:5, 8:2 and 1:0 respectively. Higher H₂ concentration helps remove the carbon layer, which might then enhance the carbon formation. However, the higher ratio of C₂H₄ to H₂ does not lead to higher productivity of CNFs since H₂ is also generated from ethylene decomposition. The maximum growth of CNFs is achieved at a C₂H₄/H₂ ratio around 5:5 under the tested conditions. Similar results have been shown by Baker [10].

Table 2 Productivities, BET surface areas, pore volumes and diameter distributions of CNF/AC composites as a function of temperature. Synthesis conditions: 1 wt% Fe/AC catalyst (iron nitrate precursor), C₂H₄:H₂ = 50:50 cm³/min, 2 h.

Samples	Reaction temperature(°C)	Productivity (g C/g Fe)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Diameter distribution	
						Diameter range (nm)	Dominant diameter (nm)
CNTs-34	500	19.1	1121	0.600	0.499	40-120	40
CNTs-33	600	61.3	742.5	0.432	0.347	50-400	200
CNTs-32	700	107.6	56.0	0.080	0.038	50-400	200
CNTs-35	800	93.5	38.5	0.011	0.026	50-400	200

The reaction temperature also plays an important role in CNF growth. Short CNFs or carbon nanospheres with nano-sized Fe particles were obtained at 500 °C. The length of CNFs increases from 600 nm to 2 µm when the temperature is increased from 500 to 600 °C. The length of the CNFs is up to 20 µm and the surface of the CNFs is less defective when the reaction temperature is 700 °C. The CNFs prepared at 800 °C do not show the characteristic round nanofibers synthesized at lower temperatures, instead of the curved fibers. As seen in Table 2, the maximum productivity was obtained at a growth temperature of 700 °C where also the least defective CNFs were obtained. The dependence of CNF productivity on the reaction temperature can be described as follows: First, the conversion of ethylene increases with increasing temperatures, i.e., more carbon will be deposited on the Fe/AC catalyst. This explains why the CNFs become longer at higher temperatures. Second, the carbon solubility and diffusion will be higher at higher temperatures. Therefore carbon diffusion through the metal particles is faster, benefiting catalyst activation and CNF growth. The BET surface areas and the total pore volumes decrease with increasing reaction temperature. This can be partly attributed to the fact that the CNFs are immobilized not only on the surface but also in the pores of the AC.

Table 3 Productivities, BET surface areas, pore volumes and diameter distributions of CNF/AC composites as a function of reaction time. Synthesis conditions: 1 wt% Fe/AC catalyst (iron nitrate precursor), C₂H₄:H₂ = 50:50 cm³/min, at 700 °C.

Samples	Reaction time (min)	Productivity (g C/g Fe)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Diameter distribution	
						Diameter range (nm)	Dominant diameter (nm)
CNTs-27	10	24.4	1013	0.575	0.467	50-250	50
CNTs-26	30	45.0	727.0	0.488	0.356	50-400	200
CNTs-20	60	84.7	184.2	0.157	0.102	50-400	200
CNTs-32	120	107.6	56.0	0.080	0.038	50-400	200

Table 3 lists the productivities, BET surface areas, pore volumes and diameter distribution of CNF/AC composites as a function of reaction time. The reaction time was varied between 10 and 120 min. The longest CNFs are up to 3 µm when the reaction time is 10 min. When increasing the reaction time to 30 min, the length of the CNFs is up to 7 µm. Meanwhile, the productivity increases from 24.4 to 45.0 g C/g Fe. Tripling the reaction time does not lead to a tripling of the productivity, meaning that the growth rate of CNFs is quite fast in the first 10 min, and then decreases. When the reaction time is 60 min, longer CNFs and higher CNF productivity were obtained. However, the diameters of the CNFs do not change. The same thing occurs when the reaction time is increased to 120 min. The length of CNFs becomes longer and the productivity of CNFs increases with increasing reaction time. The decreased growth rate could be attributed to a catalyst deactivation process. The initial decomposition of ethylene is to provide nucleation sites for the growth of CNFs. This is why the iron particles can be easily observed when reaction time is less than 30 min. Similarly, an increase of deposited carbon productivity was reported by Venegoni et al. during the first 60 min and a stable productivity is observed after 60 min [11]. After immobilization of CNFs on AC, the percentage of micropore volume in the total pore volume decrease with increasing reaction time. The micropore volume and BET surface area decrease with increasing reaction time. The immobilization of CNFs on AC with different reaction times has a significant influence on morphology of CNFs, the porosity and surface area of AC.

In conclusion, the chemical vapor deposition synthesis conditions of CNFs/AC composites have been investigated. The Fe/AC catalyst prepared with iron nitrate produces the highest productivity of CNF/AC composites, whereas the catalysts prepared using iron citrate and iron acetate lead to CNFs with smaller diameters. The highest productivity was obtained with a C₂H₄:H₂ ratio of 5:5. The reaction temperature determines the morphology and productivity of CNF/AC composites. The productivity of CNF/AC increases with reaction time, but not linearly and the CNF growth rate decreases with reaction time.

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