Direct synthesis of carbon nanofibers on modified biomass-derived activated carbon

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ABSTRACT

Carbon nanofibers were synthesized on activated carbons produced from agricultural waste using chemical vapor deposition. Importantly, iron already present in the ash content of the activated carbon was employed as a natural catalyst for nanofiber formation. The need for a wet chemical catalyst preparation step was avoided.

Activated carbon (AC) is one of the most widely-used carbon materials for adsorbents and catalyst supports. Agricultural waste such as nut shell and wheat straw, can be used to produce AC [1,2]. Recently, a hierarchically structured carbon, consisting of carbon nanofibers (CNFs) supported on AC, has been successfully synthesized by chemical vapor deposition (CVD) of ethylene on an AC-supported iron catalyst [3–6]. The resulting hierarchical carbon combined the unique properties of CNFs with those of classical AC, while maintaining chemical compatibility between these two phases. In addition, it is highly desirable that CNFs are supported on pellets since CNF in powder form is unsuitable for application in catalysts or catalyst supports [6]. The immobilisation of CNFs on AC in the way described allows the preparation of CNF-containing pellets.

The first step in the synthesis of hierarchically structured carbon is to prepare Fe/AC catalysts by an impregnation method because Fe catalyses the growth of the CNFs [3–6]. Iron is a biologically essential element and is ubiquitous in plants [7]. Therefore, it is unavoidable that biomass-derived AC would contain iron as part of the ash content. In this work, the intrinsic iron content of ACs synthesized from biomass has been directly used as a catalyst for CNF synthesis. The step involving the preparation of Fe particles on AC is therefore avoided and the overall process simplified. Our process is environmentally friendly and overall production costs are low.

ACs prepared from palm kernel shell (AC-P), coconut (AC-C) and wheat straw (AC-W) were supplied by NanoC Ltd., Malaysia. The element analyses of the raw ACs were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kronach, Germany). The compositions of the biomass-derived ACs are listed in Table 1. The total content of Fe and Ca in the biomass-derived ACs are less than 3 wt%. The rest components are silicon, potassium and other impurities. In order to open inaccessible pores, to create new pores by oxidization of carbon and widen the existing pores for a homogeneous growth of CNFs [3,8], all the ACs were calcined in a Muffle oven at 400 °C for 4 h. The calcined ACs are denoted as AC-P400, AC-C400 and AC-W400. To prepare the CNFs/AC composites, the calcined AC (200 mg) was placed in a vertical fixed bed microreactor. The microreactor was flushed with He for 2 h and a mixture of ethylene and hydrogen (the ratio of ethylene to hydrogen is 1:1) was introduced into the microreactor. Flow rates were 200 cm^3/min. The temperature was increased from ambient to 700 °C at a heating rate of 10 °C/min and maintained at 700 °C for 2 h. The CNFs/AC composites prepared from calcined AC-P, AC-C and AC-W are denoted as CNFs/AC-P, CNFs/AC-C and CNFs/AC-W.

The weight of the samples AC-P, AC-C and AC-W was measured before and after calcinations. The weight loss of AC-P, AC-C and AC-W were 5.2, 15.2 and 18.8 wt%, respectively. The BET specific surface area of the AC-P increased from 1081 to 1273 m^2/g, while the total pore volume rose from 0.365 to 0.601 cm^3/g (Table 2). However, the BET specific surface areas of the AC-C and AC-W remained approximately constant at 1200 m^2/g after calcinations. The total pore volumes of the AC-C and AC-W decreased. Correspondingly, the micropore volumes of the AC-C and AC-W also decreased slightly. The micropore volumes of the raw and calcined ACs are more than 80% of the total pore volumes. Fig. 1a and b are the secondary electron (SE) images of the AC-C before and after calcinations. Fig. 1c shows SEM image of AC-P with a

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Table 1 – Element analyses of biomass-derived activated carbons.

Activated carbon	Element analysis (wt.%)					
	C	O	N	H	Si	Fe (or Ca)
AC-P	92.42	0.82	0.35	0.46	0.71	2.91
AC-C	84.58	7.6	0.18	0.83	0.42	0.17
AC-W	81.29	8.44	0.82	1.10	1.41	1.70

Table 2 – Physicochemical properties of biomass-derived activated carbons and CNFs/AC composites.

Samples	BET specific surface area (m^2/g)	Total pore volume (cm^3/g)^a	Micropore volume (cm^3/g)^b	The product weight after CNF growth (mg)^c
AC-P	1081	0.365	0.343	–
AC-P400	1273	0.601	0.522	–
CNFs/AC-P	15	0.035	0.013	270
AC-C	1268	0.557	0.450	–
AC-C400	1189	0.495	0.422	–
CNFs/AC-C	32	0.055	0.025	271
AC-W	1228	0.752	0.595	–
AC-W400	1221	0.641	0.587	–
CNFs/AC-W	102	0.105	0.071	296

a The total pore volume is calculated when the relative pressure P/P$_0$ is 0.96.

b The micropore volume is obtained by density functional theory (DFT) method.

c The starting mass of AC is 200 mg.

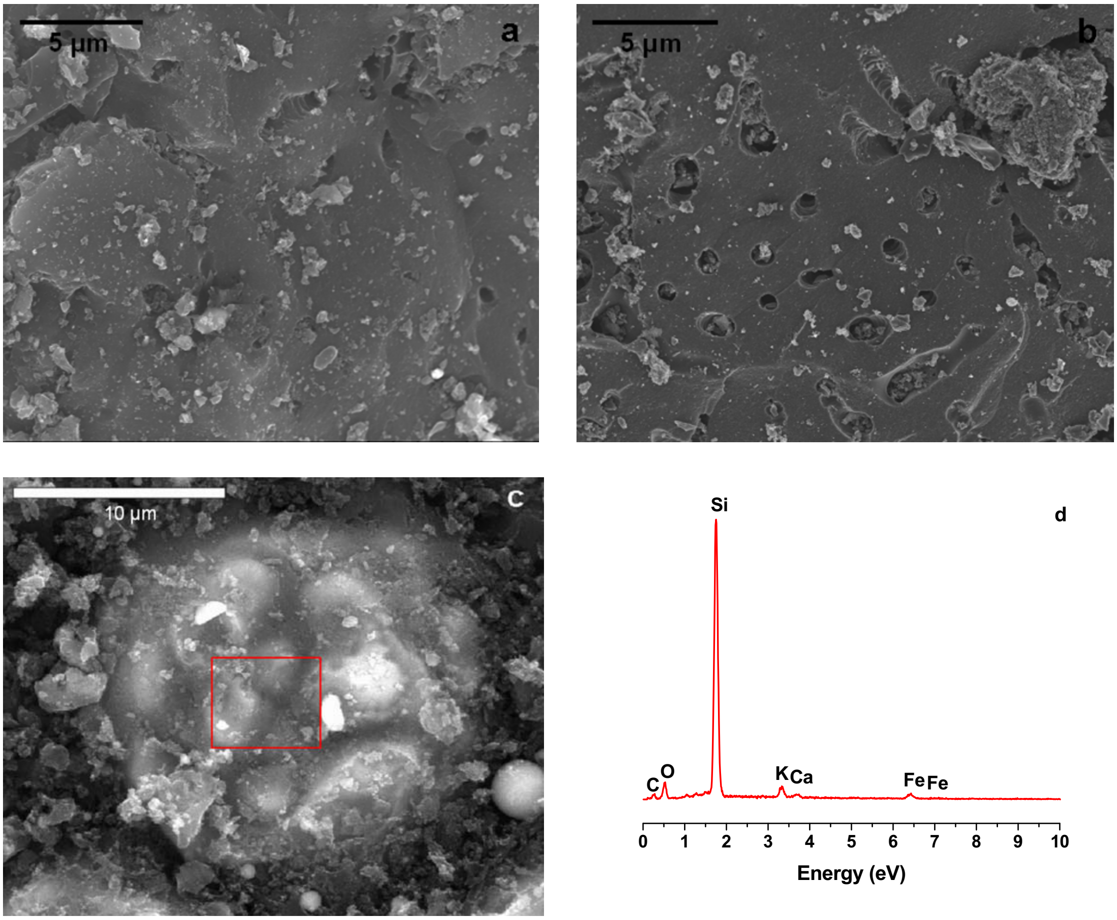

Fig. 1 – SEM images of (a) AC-C as prepared, (b) AC-C after calcination at 400 °C, (c) AC-P (the bright particles are iron, silicon, calcium and potassium elements in AC, (d) EDX profile of the selected area of (c).

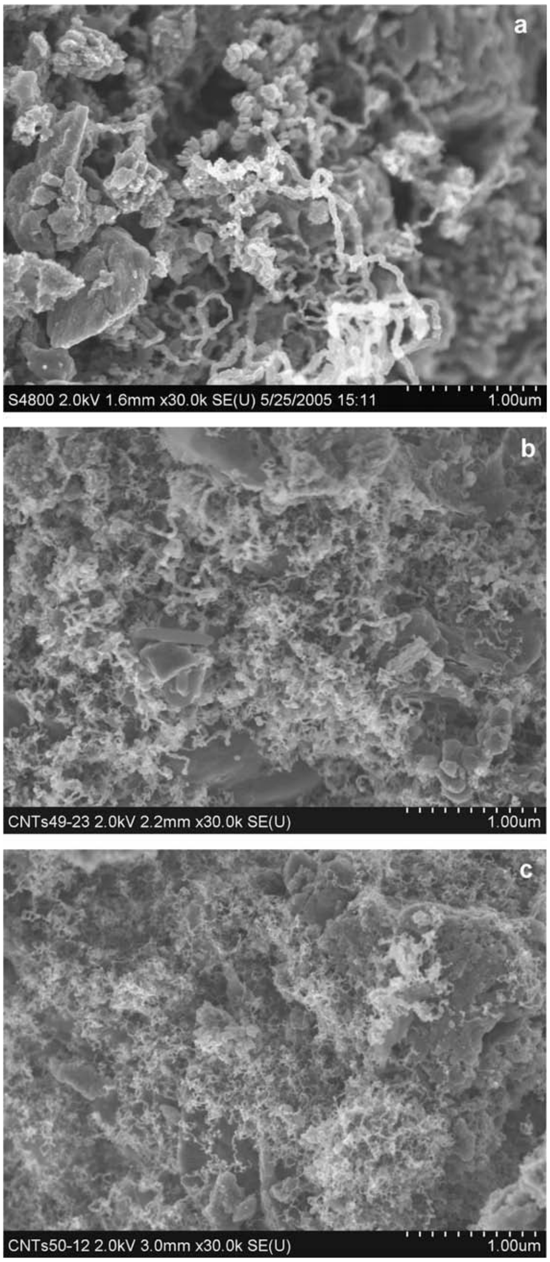

Fig. 2 – CNFs supported on the surface of (a) AC-P, (b) AC-C, (c) AC-W.

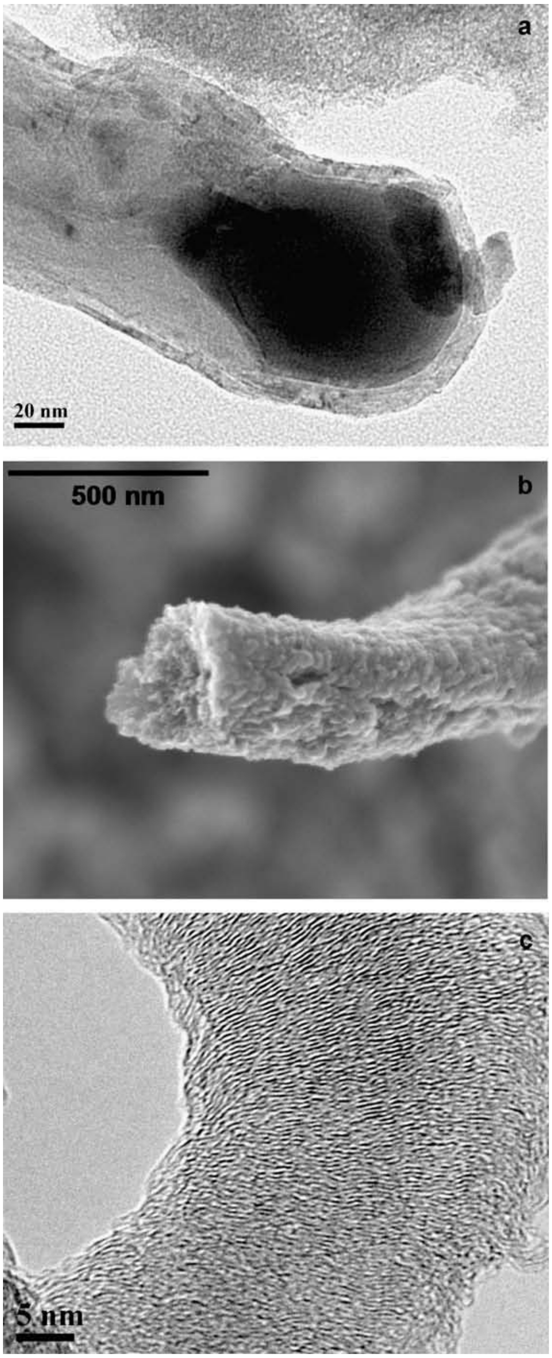

Fig. 3 – (a) TEM image of a CNF with an iron particle on the tip, (b) SEM image of a carbon nanofiber, (c) high-resolution image of a carbon nanofiber.

bright particle with a diameter of 20 μm. The energy dispersive X-ray spectroscopy (EDS) profile confirms that the bright particles are comprised of oxygen, iron, silicon, potassium and calcium elements. The element analyses indicate that there is 0.17 and 1.70 wt% iron and calcium in the AC-C and AC-P, respectively.

After the CVD process, CNFs were seen to be formed on the surface of AC-P (Fig. 2a). The CNFs tangle together and almost cover the surface of ACs. The diameters of the CNFs were typically in the range of 30–300 nm, with a small number having diameters as large as 500 nm. Fig. 2b and c indicate that CNFs also have grown on the surface of AC-C and AC-W. Fig. 3a presents a high resolution transmission electron microscopy (HRTEM) image of the tip of a CNF containing an iron particle with a diameter of about 100 nm. This means that the iron in the ash of the ACs catalyses the decomposition of ethylene and CNFs grow on ACs. The iron can be reduced in the atmosphere of hydrogen and ethylene. The rounded shape of the iron particle suggests that it had been melted to form a liquid droplet at high temperature during the CVD process. Fe particles were found to be present at the tips of most of the CNFs. The growth mechanism of CNFs has been reported to proceed via the ‘tip-growing’ model [9]. According to the model, ethylene is adsorbed and dissociated into carbon on iron particles. The steps involved in the formation of CNFs on AC are as follows: (a) reduction of iron particle with H_2, (b) dissociate chemisorption of ethylene at a certain set of faces of iron particles, (c) diffusion of carbon species produced during the decomposition reaction, through the catalyst particle, and (d) precipitation of solid carbon at other metal faces to create a fibrous structure [10]. It is generally believed that carbon diffusion through the metal particles is the rate-controlling step in the CNF growth process [10].

Fig. 3b shows that the surface of the CNF is rather rough, which is similar to our earlier results [3–6]. Fig. 3c shows the HRTEM image of a single CNF with a diameter about 30 nm. The carbon layers are not well ordered but nearly perpendicular to the axis of CNF. During the CVD processing, the weight of the ACs increased from 200 to 270, 271 and 296 mg for AC-P, AC-C and AC-W (Table 2), respectively. The yield of CNFs on AC was found not to be proportional to the amount of iron in the starting AC, which suggests that the iron in the AC leads to the catalytic decomposition of ethylene, but does not determine the productivity of CNFs on AC. The reason might be that the iron content can be buried in the bulk of AC and ethylene can not reach so deeply and not all the iron content plays a role in the CNF growth.

Table 2 also lists the BET specific surface areas, total pore volumes and micropore volumes of the CNFs/AC composites. The BET specific surface areas of the CNFs/AC composites decreased drastically from approximately around 1200 to 15, 32 and 102 m^2/g for the AC-P, AC-C and AC-W. The total pore volumes and micropore volumes also decreased a lot. The percentage of micropore volumes in the total pore volumes decreased to 37%, 45% and 68%. The dramatic decrease of BET specific surface areas, total pore volumes and micropore volumes is due to the CNF growth in the pores of ACs. The CNFs fill some of pores of ACs, especially the micropores of ACs. This phenomenon is consistent with our previous results [3–6].

In summary, ACs prepared from biomass can be used directly as catalysts to synthesize the hierarchically structured carbon, without the need for an iron incorporation step, since the biomass already contains iron. This iron, present in the ash content of the ACs, acts as a “natural catalyst” and can catalyse the formation of CNFs from ethylene on biomass-derived ACs.

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