Novel solid-cored carbon nanofiber grown on steels substrates in ethanol flames

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In the present work, we fabricated a solid-cored and less-ordered carbon nanofibers (CNFs) on carbon steels and low-alloy carbon steel substrates by using ethanol flames. The diameter of the CNFs ranged between 20 and 250 nm. A "solid-cored mechanism" was proposed to explain the present results, which suggested that the strong affinity of Fe for carbon resulted in the fast diffusion inside the Fe-contained particles and forms the solid-cored CNFs.

This is a continuation of our previous research on synthesis of carbon nanotubes (CNTs) by using ethanol flames [1, 2]. Previously, we reported that CNTs, including well-aligned CNTs, have been successfully produced on Ni-contained austenitic stainless steels within ethanol flame environment. Recently, a novel solid-cored carbon nanofiber (CNF) was found when using carbon steel or low-alloy steel as the substrate. In the present paper, the character of the CNFs and the growth mechanism are discussed.

Generally, both CNTs and CNFs are considered to be promising nanomaterials for applications, such as field emission [3], hydrogen storage [4], reinforcement of composites [5], and electrodes for fuel cell [6], because of their unique mechanical and physical properties.

However, up to now, the terminology for CNTs and CNFs are not clearly defined, which means that a "fiber" is actually a "tube" [7–9]. Historically, the term "nanofiber" is used for both CNTs and CNFs with or without a hollow core. Sometimes, a highly graphitic structure with the basal carbon planes parallel to the tube axis is called a CNT. The CNFs are the other structures, such as the graphitic planes incline to the axis and leave a small or no central channel (called "herringbone"), or multi-walled carbon nanotubes (MWCNTs) [10–12].

In the present paper, the term CNTs is defined referring to the filament with a center core as described earlier, while the term CNFs is defined as a filament without a central channel or just a solid-cored fiber, regardless of the graphitic wall structures.

The synthesizing process for the solid-cored CNFs is almost the same as described in the previous work [1, 2]. However, only the carbon steels and low-alloy carbon steels were used as the substrates with size 20 mm × 10 mm × 10 mm or larger. Table I lists the chemical compositions of the substrates. The sampling surfaces were first mechanically polished to different levels of roughness by using different grade of abrasive papers. And then the surfaces were or were not pretreated by dipping in a solution of 5 ml pure nitric acid (HNO_3) + 100 ml absolute ethanol (C_2H_5OH) for several seconds. The total synthesizing process generally was not strictly limited, which implied that the CNFs were easily synthesized in an ethanol flame.

Microstructures and morphologies of CNFs were examined by using Japan Hitachi S-570 scanning electron microscope (SEM), Japan JEOL JEM2010 conventional transmission electron microscope (TEM) and JEOL JEM2010FEF high-resolution transmission electron microscope (HRTEM) installed with an electron energy loss spectrometer (EELS) and Gatan CCD cameras, respectively. The laser Raman spectra were performed in England Renishaw-1000 laser Raman spectroscopy instrument in the back-scattering configuration at room temperature. The excitation source is 514.5 nm Ar-ion laser line.

Fig. 1 illustrates the SEM morphologies of the combustion materials grown on low-carbon steel (Q235), which shows the disordered and randomly fibrillous structures same as the other observations [12–14], and piled-up imbricately in a large volume. However, TEM observation revealed that the combustion fibrillous material had a structure with a completely solid-cored structure called carbon nanofibers, as shown in Fig. 2. Some of them even exhibited a helical shape. Repeating the experiments using the other carbon steels or low-alloy carbon steels, the similar results was obtained.

The diameter of the CNFs varied in a large range, the smallest was 20 nm, while the largest was around 250 nm, and the length could be several tens of microns. Generally, a particle was embedded at one end of a fiber, which indicated that the CNFs followed the "deposition–diffusion–nucleation–growth" mechanism [10, 15, 16]. The smaller particles tended to induce smaller diameter fibers, whereas larger ones for larger diameter fibers. EELS measurements showed that the particles contained elements Fe and O (Fig. 3). Selected-area electron diffraction (SAD) analysis revealed that the particles were mainly iron oxide Fe_3O_4(Fig. 4). Further HRTEM examination showed that the fiber consisted of disordered graphitic layers (Fig. 5). Raman spectra had a large D-band at 1346 cm^{-1} (Fig. 6), which was induced from a disorder-induced phonon mode.

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TABLE I Chemical compositions of the substrates

	Chemical compositions (wt.%)						
Substrates	C	Si	Mn	Cr	S	P	Fe
Q235	0.100	0.120	0.400	–	0.020	0.073	Bal.
45#	0.46	0.25	0.67	–	0.034	0.029	Bal.
T8#	0.82	0.33	0.71	–	0.035	0.026	Bal.
40Cr	0.37–0.44	0.17–0.37	0.5–0.8	0.8–1.1	–	–	Bal.
16 Mn	0.12–0.2	0.2–0.55	1.2–1.6	–	0.045	0.045	Bal.
65 Mn	0.62–0.70	0.17–0.37	0.9–1.2	0.25	0.035	0.035	Bal.

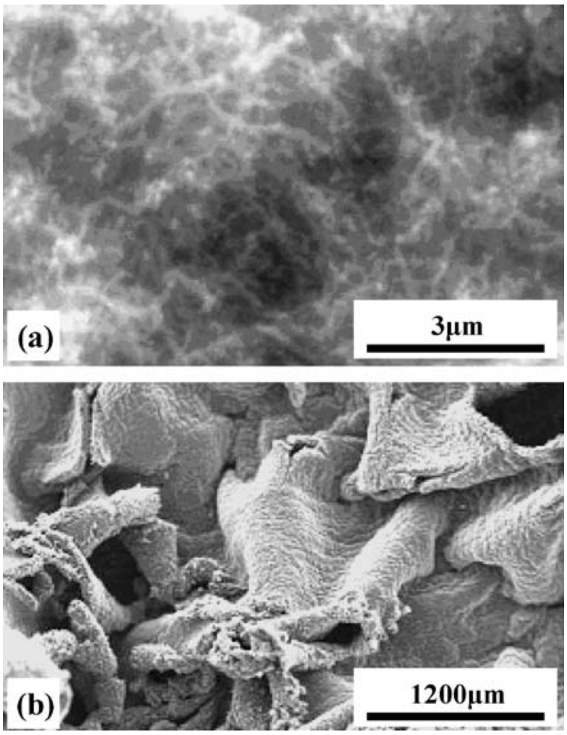

Figure 1 SEM morphologies of CNFs grown on Q236 low-carbon steel substrate: (a) high magnification and (b) low magnification.

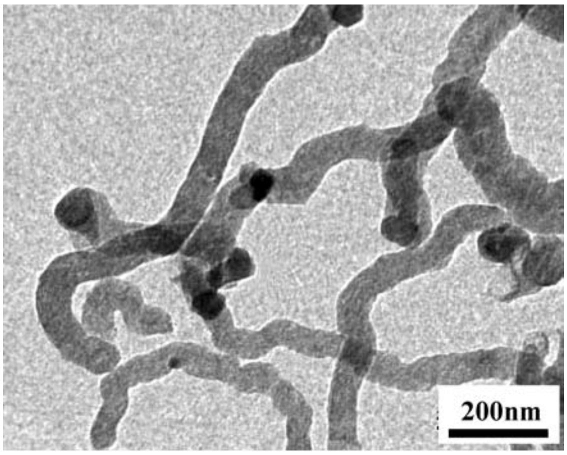

Figure 2 TEM micrographs of CNFs grown on Q236 low-carbon steel substrate.

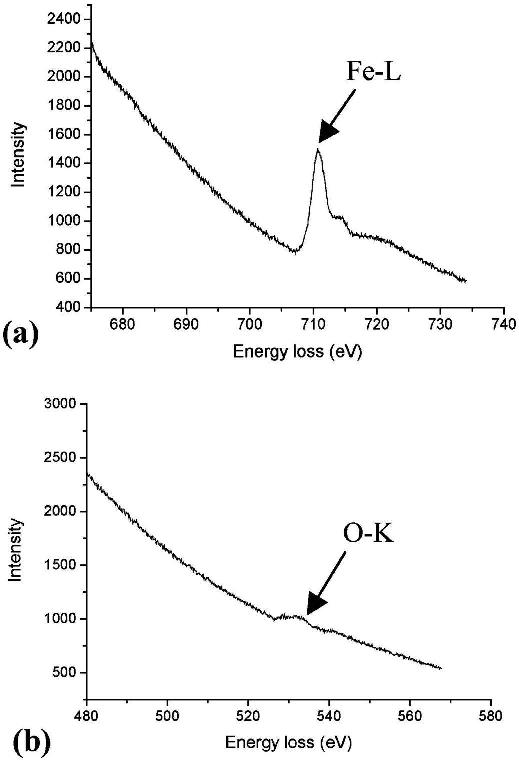

Figure 3 EELS chemical compositions of the particle: (a) Fe element and (b) O element.

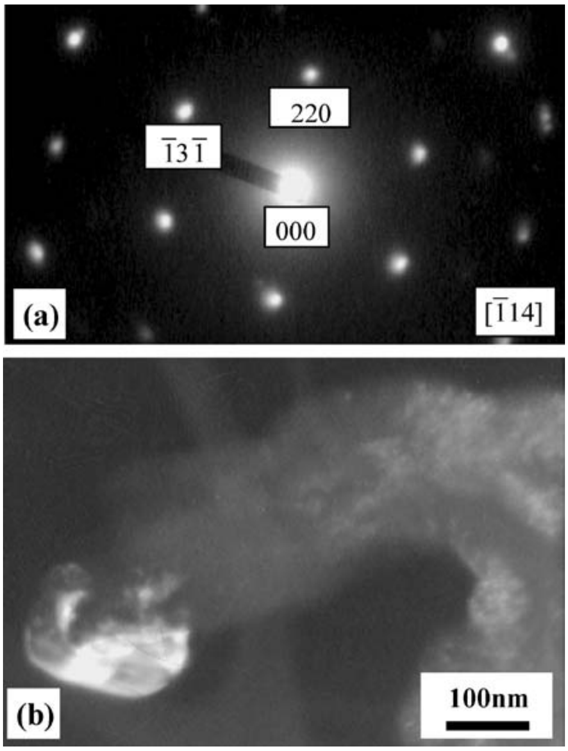

Figure 4 TEM micrographs of iron oxide Fe_3O_4 particle embedded at the end of CNFs grown on 65 Mn steel substrate: (a) $[\bar{1}14]$ axis SED pattern and (b) (2 2 0) dark field image.

According to the above results, the present CNF has two characters. (1) It always grows on the carbon steels or low-alloy carbon steel substrates and relates to the Fe-contained particle. (2) It possesses a disordered and solid-cored microstructure, which is different from the so-called vapor-grown carbon nanofibers (VGCNFs) or hydrocarbon-pyrolyzed CNFs. The VGCNFs generally have a hollow core and high-crystallinity graphite filament surrounded by a pyrocarbon layer with low-graphite crystallinity [17] and the hydrocarbon-pyrolyzed CNFs have a “herringbone” wall [6, 12] or “fishbone” wall [16] or a highly crystalline wall [6, 8].

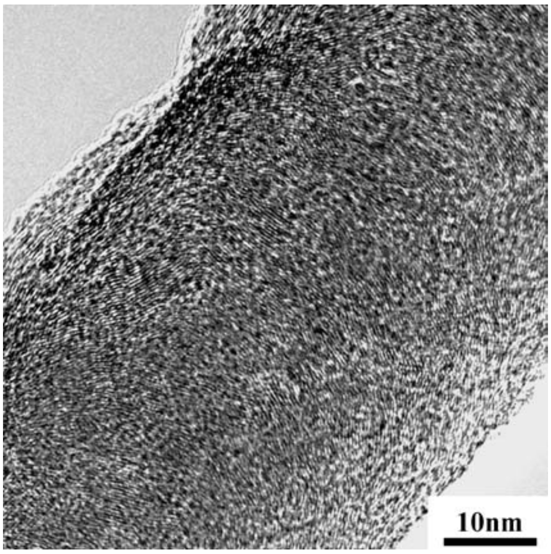

Figure 5 HRTEM micrographs of CNFs grown on Q236 low-carbon steel substrate.

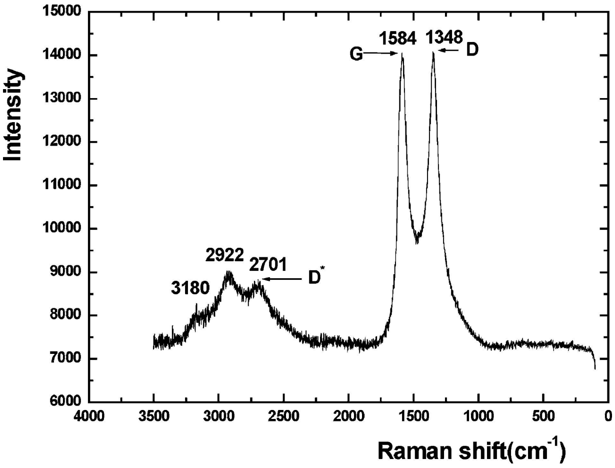

Figure 6 Raman spectra of the CNFs grown on Q236 low-carbon steel substrate.

Primarily, a "solid-cored mechanism" for the CNFs growth is proposed based upon the theory that "Fe has a strong affinity for carbon," which is well known for iron carbide precipitation in steels and alloys [18]. That is to say, when pyrolyzed carbon atoms formed in an ethanol flame gets deposited on the Fe-containing particle, it will not only migrate along the external particle surface, but will also diffuse easily through the interior of the particle due to strong affinity, and will then grow the solid-cored CNFs. In fact, this diffusion phenomenon leads to the disorder graphitic microstructure within the CNFs. Unfortunately, this mechanism can not be used to explain Fe-catalyzed CNTs growth by using arc-discharge, chemical vapor deposition (CVD) and other methods [10, 19, 20]. The reason may be due to the difference in ethanol flaming conditions. Further research is being proceeded.

In conclusion, ethanol flame provides a special condition for growing solid-cored and low-ordered graphitic CNFs on carbon steel substrates, and the Fe-containing particles are considered to be the key factors in controling the process.

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