Letters to the Editor

Synthesis of carbon nanotubes by electrochemical deposition at room temperature

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Carbon nanotubes are finding increasing commercial applications in modern technologies, for example, composite materials, electrochemical devices, hydrogen storage, field emission devices, and nanoscale electronic devices [1]. Wide applications of carbon nanotubes are based on their unique physical and mechanical properties, which show the high electrical and thermal conductivities, and high mechanical strength along the tubular axis [2–4].

Carbon nanotubes are normally produced by either a carbon arc-discharge technique [5,6] or a pyrolysis of hydrocarbon gases on particles of transition metals such as Fe, Ni, and Co in a chemical vapor deposition (CVD) reactor [7,8]. For the carbon nanotubes produced from a CVD technique, their diameters are controlled by the sizes of the catalytic particles. The growth mechanism of the carbon nanotubes from a CVD process has been the subject of some controversy, particularly regarding to the active catalytic state of the particles. Key steps include the absorption and decomposition of hydrocarbon molecules on the exposed metal surface to produce carbon species which dissolve into and diffuse through the underlying bulk, ultimately precipitating at the rear surface of the particle to form the carbon nanotubes [9–12].

At the same time, in recent years, more attention has been paid to electrochemical deposition technique for manufacturing thin films and devices due to its simplicity, its low capital equipment cost, and its ability to be scaled up for large production [13–16]. So far, it has not been reported that carbon materials can be deposited or plated through an electrical process using an organic solvent.

In this work, an electrochemical deposition technique has been employed to produce carbon nanotubes from organic solvents at room temperature [17]. Transition metal nanoparticles (Ni and/or Fe) were coated on the electrodes to provide the nucleation sites for the formation and growth of carbon nanotubes. The microstructure characterization of the carbonaceous deposits has been carried out with SEM, TEM, and energy dispersive X-ray spectroscopy (EDS).

A standard three-component electrochemical cell was used as the electrochemical reactor for the carbonaceous depositions. A saturated calomel electrode was used as reference electrode. Two silicon wafers coated with 50:50 Fe/Ni alloy nanoparticles [12] were employed as counter electrode (anode) and working electrode (cathode), respectively. A mixture of 40 vol% methanol (CH_3OH) and 60 vol% benzyl alcohol ($C_6H_5CH_2OH$) was used as the electrolyte. The sizes of counter and working electrodes were about $2.5 \text{ cm} \times 2.0 \text{ cm}$. The distance between cathode and anode was kept at 5 mm, which was precisely controlled by a SiC spacer. The potential difference applied between the anode and cathode was kept nominally at 1000 V. The depositions were carried out at room temperature and

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magnetic stirring was employed to achieve a uniform distribution of carbonaceous deposit on the cathode. No carbonaceous deposits were found on the anode. After deposition, the samples were removed from the solution and allowed to air dry. The morphologies of the deposited carbon materials and their overall distribution on the substrates were examined using a JEOL JSM-6400F SEM. The compositional analysis of the deposited materials was carried out using an Oxford EDS system. Internal microstructure of deposited nanotubes was examined using a Philips EM 420 TEM operated at 120 kV.

Fig. 1(a) is a low magnification SEM image of the carbonaceous deposit on a Si substrate coated with Fe particles, showing that the deposited carbonaceous material consists of bunches of nanotubes distributed over the entire substrate. A thin layer of amorphous carbon (labeled by "A") can be deposited on the silicon substrate while the carbon nanotubes (indicated as "F") are grown from the cracks of the carbon film. This observation suggests that the carbonaceous deposits of the electrochemical reaction can be either in the form of films or nanotubes. It has also been observed that in the electrochemical reactions the catalytic particles play an important role in stimulating the growth of the carbon nanotubes. More detailed growth phenomenon of the carbon nanotubes is shown in Fig. 1(b), indicating that during the electrochemical process, carbon nanotubes like to form bundles and have a preferred growth direction, which is the direction of the local electrical field on the cathode. Fig. 1(c) shows a high resolution EDS spectrum of the carbon nanotube bundles, confirming that the deposits are carbonaceous materials. Note that in the spectrum, the silicon peak is coming from the substrate and the oxygen peak is coming from the oxidization of the silicon wafer.

Fig. 2(a) is another low magnification SEM image showing the presence of two different morphologies of carbon nanotubes found in the electrochemical carbonaceous deposits. It could be seen together with nanotubes grown from the catalytic particles on the cathode (labeled as "F") and the single nanotubes exist (indicated as "S") with a random orientation. The single nanotubes vary widely in diameters from 50 to 500 nm, and their length measures in the range 1–20 μm. Fig. 2(b) shows the bundles of carbon nanotubes, grown around the cracks of amorphous carbon thin film. These nanotubes in a bundle are parallel aligned and have similar diameter of 100 nm and length of 3–5 μm, respectively. TEM analysis has been employed to identify the internal structure of the carbon nanotubes produced from the electrochemical deposition method. The TEM micrograph, shown in Fig. 2(c), confirms that the carbon nanotubes observed in SEM previously have a hollow core structure (indicated by arrows). The sizes of the nanotubes measured from the TEM micrographs range from 50 to 500 nm in length and 20 to 60 nm in diameter.

As mentioned previously, the carbon nanotubes can be produced by a CVD method. In a CVD process, catalyst particles play a key role in the carbon nanotube growth. It first breaks down the hydrocarbon molecules at high
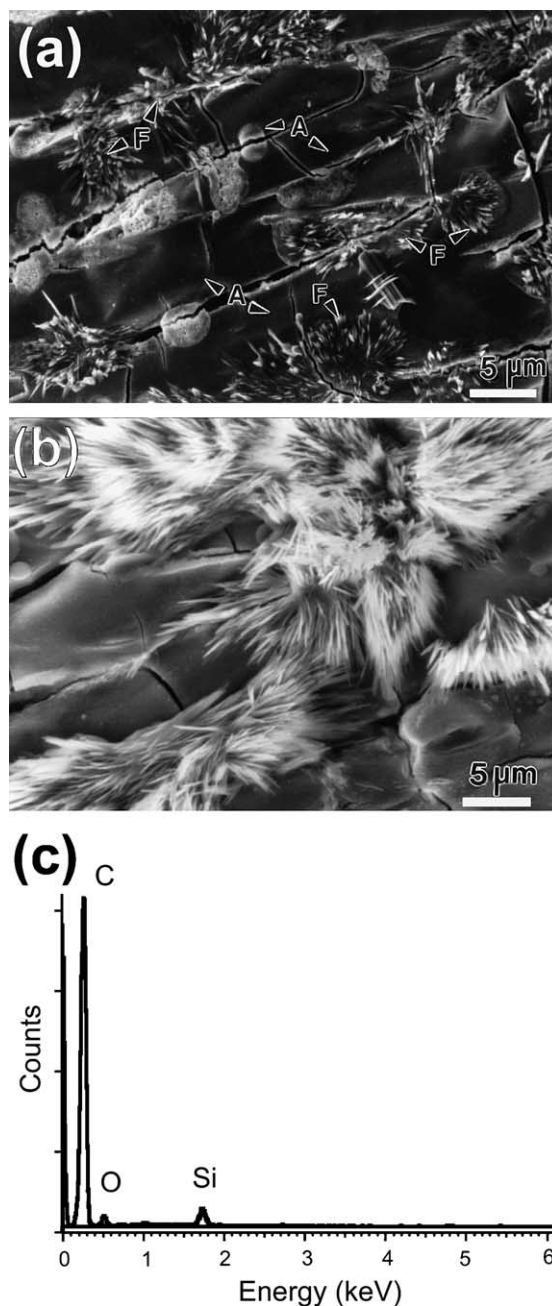

Fig. 1. SEM micrographs of carbonaceous material deposited on a Si substrate coated with Fe nanoparticles showing: (a) morphology and distribution of carbon nanotubes, (b) bundles of carbon nanotubes protruding out the surface of the cathode and (c) an EDS spectrum of the carbon nanotube bundles.

temperature, and then the carbon atoms diffused into the catalytic particles. It was pointed out that the diffusion of carbon atoms through the catalytic particle is the rate-limiting step for carbon nanotubes or nanofilament growth [6–8]. The temperature gradient of the hotter leading surface and the cooler rear surface of catalyst particle is assumed to be the driving force of the nanotube growth. The driving force for the carbon nanotube growth in an electrochemical deposition is likely to be the electrical field near the catalytic particles. It has been noticed that a
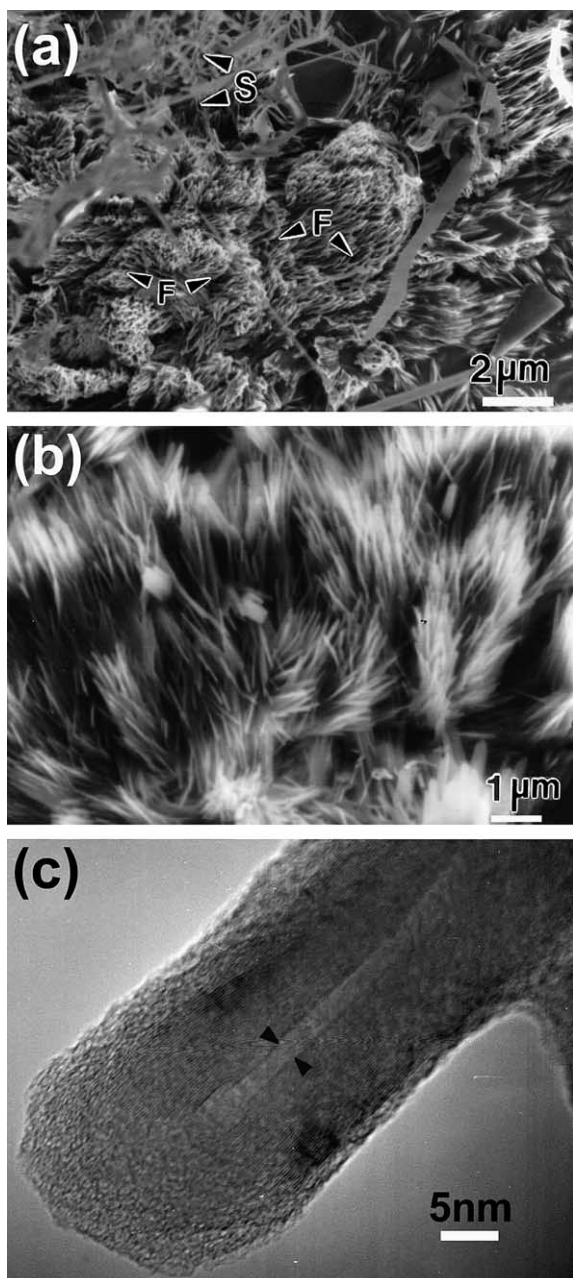
Fig. 2. Electron microscopy images of the carbon nanotubes produced from an electrochemical process at room temperature showing: (a) SEM image of two different types of the carbon nanotubes (arrows "s" indicating a carbon networks with random orientation and arrows "F" illustrating bundles of carbon nanotubes in which the tubes are parallel aligned), (b) SEM image of the bundles of the carbon nanotubes with a parallel orientation and (c) TEM image of one of the carbon nanotubes (arrows indicate the hollow core of the tube).

mixture of 40 vol% methanol and 60 vol% benzyl alcohol provides the best condition for the nanotube formation and growth. Pure methanol with relative high electrical conductivity yields large amount of amorphous carbon materials without carbon nanotube growth as shown in Fig. 3(a) in a few hours. Pure benzyl alcohol, on the other hand, has a relative low electrical conductivity, and using benzyl alcohol as the electrolyte will produce a thin layer
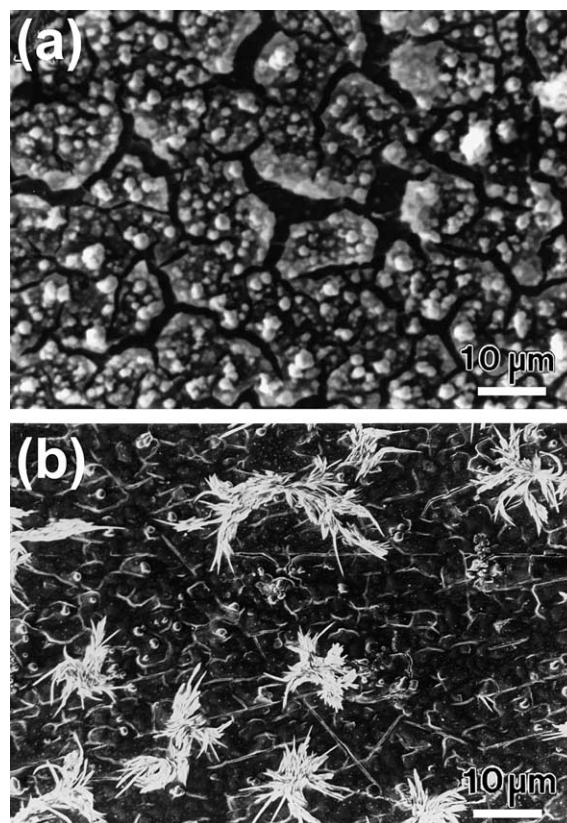

Fig. 3. SEM images of the carbonaceous deposits from different electrochemical processes demonstrating: (a) a thin amorphous carbon layer being deposited when pure methanol is used as the electrolyte and (b) a thick layer of amorphous carbon with some bundles of carbon nanotubes being deposited when pure benzyl alcohol is used.

of carbonaceous film with some bundles of carbon nanotubes as shown in Fig. 3(b). In this case, the deposition process will take about 60 h for the formation of the carbon nanotubes.

In conclusion, carbon nanotubes have been produced by an electrochemical deposition method from organic solutions at room temperature. The formation and growth of carbon nanotubes are stimulated by the transition metal catalysts, such as iron and/or nickel nanoparticles. It has been found that the electrochemical deposition conditions have a strong influence on the growth morphology of the carbon nanotubes. SEM characterization shows that the diameter of nanotubes is of the order of 100 nm, and the length of nanotubes can be up to 20 μm, depending on the size of catalyst particles. Moreover, the TEM analysis confirms the hollow structure of deposited nanotubes.

Acknowledgements

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Accurate measurement of interlayer spacing value of carbon fibers using a silver foil as an internal standard

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The interlayer spacing, d_{002}, of a carbon material is an important structural parameter that measures the perfection of carbon-layer stacking of a particular carbon material [1–4]. To accurately determine the interlayer spacing, the standard specification for the practical X-ray diffractometry thus strongly recommends the use of silicon as an internal standard in the form of an admixture with the pulverized carbon samples [5]. It is however a practical situation, particularly when fiber samples are subjected to a measurement, that a silver foil is conveniently used, being inserted in a fiber bundle as an internal standard because the pulverization of tenacious fiber samples is sometimes troublesome or time consuming.

Considering this practical situation, we tried to examine the accuracy of the d_{002} values of MP-based carbon fibers when a silver foil is used in comparison with when silicon powder is used as the internal standard material. The results show that the position of silver foil within the fiber bundle and the choice of the d_{111} spacing value of silver foil in JCPDS file influence much on the determined value of the interlayer spacings.

The fiber samples were Thornel P-25, P-55, P-75, P-100 and P-120, being kindly obtained from the manufacturer. The diffractograms were recorded in transmission mode using Ni-filtered CuK$_\alpha$ radiation ($\lambda = 0.154184$ nm) on a Nanostar (Bruker, Germany) equipped with 2D area detector, operating at 40 kV and 35 mA. Fiber bundles were mounted as shown in the bottom of Fig. 1 and the thickness of sample was kept at 0.3 mm. When the difference in the diffraction angle between the 002 reflection of

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