

***In-situ* Cu₂O formation on amorphous carbon nanotubes induced by electron beam**

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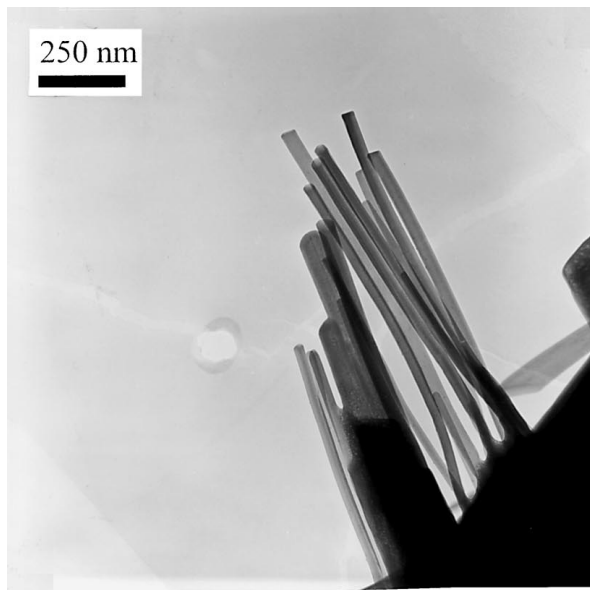
Carbon nanotubes exhibit unique properties such as biocompatibility, mechanical stiffness, electrical conductivity, and field emission properties and consequently have drawn a great deal of interest in materials research recently for potential applications in catalysis, microelectronics, microbiology, medicine and gas storage [1–11]. In recent research by Shih and coworkers [12, 13], aligned amorphous carbon and carbon nitride nanotubes have been successfully grown on porous anodic alumina membranes by electron cyclotron resonance (ECR) plasma excitation. The advantages of ECR plasma include low deposition temperature, low ion damage, high plasma density, and contamination-free depositions. A wide variety of amorphous carbon nanotubes were prepared in the anodic alumina template with different pore sizes.

The ECR plasma system used in this work has been described elsewhere [14, 15]. Briefly, the plasma is generated by a microwave excitation of 2.45 GHz using a magnetron through a waveguide and perpendicularly fed into an 875 Gauss magnetic field to achieve the ECR condition. The porous anodic alumina membranes were prepared by anodizing of aluminum sheets (purity 99.99%) at a cell voltage of 15–100 V in sulfuric or phosphoric acid solution for 2–10 h [16–18]. The membranes are 50–80 μm thick and consist of a packed array of parallel, straight, uniform channels with diameters 30–230 nm. The porous anodic alumina was then put in the ECR plasma excitation system. The base pressure in the vacuum chamber before deposition was about 6.7×10^{-4} Pa. The porous anodic alumina substrate was first cleaned by Ar ions under 800 W microwave power and 875 G magnetic field for 1 min. Subsequently, a mixture of acetylene (C₂H₂) and Ar in a ratio of 4 : 1 were introduced into the chamber and the pressure remained at about 1 Pa during the deposition. A d.c. bias of 300 V was applied to the substrate and the total deposition time is 2 min.

Characterization of the amorphous carbon nanotubes was carried out by transmission electron microscopy (TEM) along with electron energy loss spectroscopy (EELS). Preparation of the amorphous carbon nano-

tubes for TEM observation was made by dissolving the alumina membranes with 5 wt% KOH solution and then picked up by a 200 mesh Cu grid. The bright field image and associated selected area diffraction pattern of the amorphous carbon nanotubes prepared by the aforementioned method is shown in Fig. 1, in which the measured diameter of the nanotubes ranges from 30 to 65 nm. The diffraction pattern with an inner diffused ring indicates that the nanotubes consist of amorphous carbon [19]. The EELS spectrum of the amorphous carbon nanotubes is shown in Fig. 2, from which the core-loss peaks of the carbon K edge can be readily identified. Compared with the EELS spectra of the three allotropes of carbon, i.e., diamond, graphite and amorphous carbon, reported by Egerton and Whelan [20], it is found that the carbon K edge located at 284 eV of the nanotubes is the same as that of graphite and amorphous carbon. Unlike either graphite or amorphous carbon, however, the relative peak height at 284 eV in the spectrum of Fig. 2, which reflects the density states of π -electrons, is far larger than the subsequent peaks due to the σ -electron excitations located at 295 eV [20]. The unusually high density of π -electrons in the amorphous carbon nanotubes suggests that they are chemically active and likely to have better electric conductivity than graphite.

When the nanotubes were exposed to the electron beam under a current density of 1.1×10^{-7} A m⁻² for 2 min, they began to wiggle and the tip of the nanotubes with sharp edges became gradually rounded. After the nanotubes were irradiated by the electron beam for 10 min, it was observed that small clusters started to nucleate and grow in the center of the nanotubes as shown in Fig. 3a. In contrast to the amorphous carbon nanotubes in Fig. 1, the selected area diffraction pattern, Fig. 3b, of the nanoclusters ranging from 5 to 20 nm, reveals that they are crystalline. The diameters of the diffraction rings were measured to be 11.5 : 14.0 : 16.5 : 23.0 : 27.5 nm for the first five reflections that give a ratio of the reciprocal of plane spacing as 1 : 1.22 : 1.41 : 2.0 : 2.35. These ratios correspond to the (110), (111), (200), (220), and (113)



(a)



(b)

Figure 1 TEM micrograph of the carbon nanotubes (a) and the corresponding selected area diffraction pattern (b), indicating the amorphous nature of the carbon nanotubes formed in anodic alumina template.

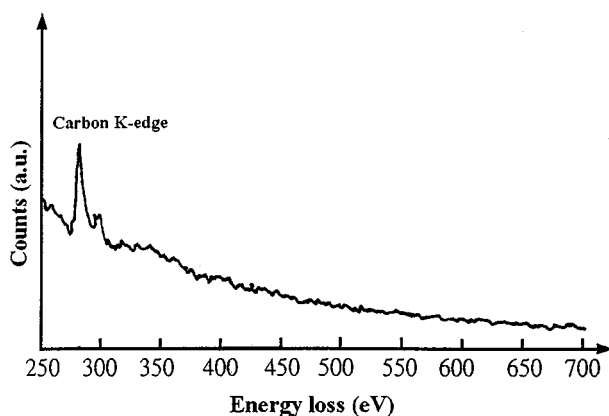
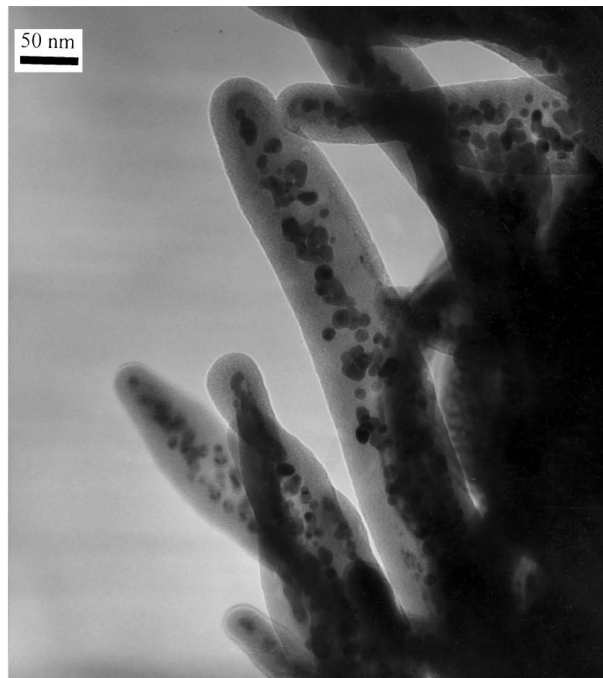
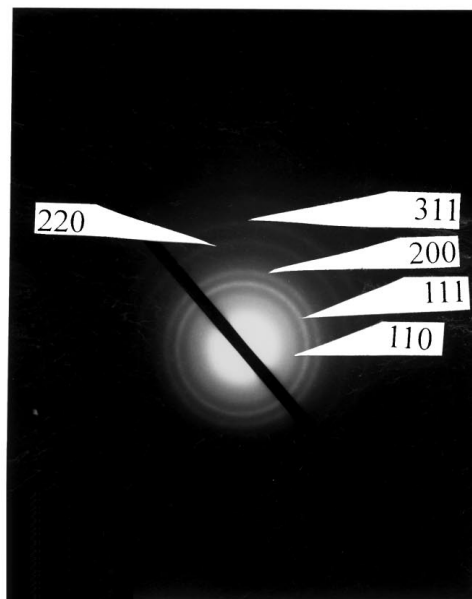


Figure 2 The electron energy loss spectrum of the carbon nanotubes synthesized in anodic alumina template shows that the density state of π -electrons (284 eV) is far higher than that of σ -electrons (295 eV) and suggesting that the carbon nanotubes are chemically more active than graphite.

reflections of a cubic Bravais lattice with lattice constant of 0.427 nm [19]. On the basis of the observed reflections and the measured plane spacing as listed in Table I [21], the nanoclusters are identified to be Cu_2O .



(a)



(b)

Figure 3 TEM micrograph of the carbon nanotubes extracted from anodic alumina template upon exposure to the electron beam for 10 min (a) and the corresponding selected area diffraction pattern (b), proving that the nanoclusters are essentially Cu_2O resulting from a reaction between the trapped oxygen in the carbon nanotubes and the sputtered copper from the Cu-grid.

It is first surprising to see the presence of Cu and O in the amorphous carbon nanotubes, in particular, none of them is detected in the EELS spectrum of Fig. 2. According to the argument of Egerton [22], the minimum detectable concentration of O within a 50 nm thick carbon matrix is estimated to be about 1.05 at%. Therefore the amount of oxygen in the amorphous carbon nanotubes must be below 1.05 at%.

As shown in Fig. 1, the amorphous carbon nanotubes when picked up by a Cu grid from the 5 wt% KOH solution during TEM specimen preparation tend to lay on the edge of the Cu grid. The Cu grid was thus constantly

TABLE I Miller indices and interplanar spacings of the nanoclusters and Cu₂O

Nanoclusters		Cu ₂ O	
<i>hkl</i>	<i>d</i> spacing (nm)	<i>hkl</i>	<i>d</i> spacing (nm)
110	0.302	110	0.302
111	0.248	111	0.247
200	0.211	200	0.214
220	0.151	220	0.151
311	0.126	311	0.129

under the bombardment of electron beam during TEM observation. Electron beam evaporated Cu can readily occur if the Cu grid is bombarded by the high-energy electrons of 80 keV for too long [23]. When the evaporated Cu redeposited on the amorphous carbon nanotubes, it may react with the trace oxygen in the nanotubes and thus form the Cu₂O nanoclusters. Since the precursors of C₂H₂ and Ar used for production of the amorphous carbon nanotubes do not contain O, it must come from other sources. One possibility is due to the sputtering of the porous anodic alumina which typically contains crystalline water, e.g., Al₂O₃ · H₂O or Al₂O₃ · 3H₂O, by the Ar plasma during deposition. It is also likely that the oxygen was introduced into the nanotubes during dissolution of the alumina in the 5 wt% KOH aqueous solution as the nanotubes are chemically active as suggested from the EELS analysis.

Although the research of carbon nanotubes produced by a variety of deposition techniques has been studied extensively recently, the presence of oxygen and its content in the carbon nanotubes have never been reported before. The current research result clearly demonstrates that the presence of oxygen in the carbon nanotubes is possible. In addition, it seems feasible, from the standpoint of analytical chemistry, to detect quantitatively the oxygen content lower than 1.05 at% in a material by the *in-situ* formation of Cu₂O during TEM observation.

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