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Short communication

Purification of carbon nanotubes using anodic oxidation in a solid polymer electrolyte (SPE) cell

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1. Introduction

Iijima [1] reported that the soot formed during the carbon arc discharge method used to produce C_{60} and other fullerenes contained carbon nanotubes (CNTs). As a result, an international and multidisciplinary research field has been developed, which has produced a variety of elongated carbon cage-like materials that have implications for current and future technology [2–4]. The synthesis, purification, properties, manipulations and, more recently, the chemistry of nanotubes are all the subjects of intensive investigation. No purification method that fulfils all requirements for technical processing of CNTs is currently available. Transition metal catalysts, fullerenes, graphitic carbon, amorphous carbon and carbon nanoparticles are the main impurities in CNTs. Among these, metal catalysts and fullerenes are relatively easy to remove; however, graphitic carbon, amorphous carbon and carbon nanoparticles are more difficult to eliminate because their inactivity is similar to that of CNTs [5, 6]. Moreover, impurities from different processes are different in composition and properties and depend on the synthesis methods, reaction time, types of catalyst and carbon source employed.

Although there are many suggested methods of purification of CNTs, oxidation with concentrated HNO_3 or HNO_3–H_2SO_4 is still widely used. However, this method may cause intercalation and partial exfoliation in the CNTs [7], and the mass reduction in the following washing steps with deionized water is much higher. Attempts have been made to overcome these drawbacks by changing the oxidant and adding catalyst. John et al. [8] reported a gas-phase purification method for raw materials that incorporates a chlorine, water and hydrogen chloride gas mixture to remove unwanted carbon. The yields indicate a uniquely selective carbon surface chemistry that prevents etching of the nanotubes. Lixin Hai et al. [9] introduced a new method in which $K_2Cr_2O_7$ was used as the oxidising agent to purify nanotubes. More recently, the role of ultrafine gold particles has assumed importance in view of the report of Mizoguti et al. [10]. Ultrafine gold particles may catalyse the oxidation of the impurities at lower temperature.

Electrolytic anodic oxidation has been used successfully in the purification of carbon fibres. The procedure is easy to control, mild and quite clean. However, it demands a large anode chamber. The CNTs are usually in a relative small batch. As a result, a compact structure like an ion exchange membrane cell is more suitable. In this study we attempt to transplant the anodic oxidation procedure to the purification process for CNT and carry out it in a SPE cell. The experiment results show that purification of CNTs by anodic oxidation in a SPE cell is practicable.

2. Experimental details

2.1. *Materials*

Raw multiwalled carbon nanotubes were fabricated in a tube furnace with a Ni-catalyst where ethylene gas was used as a carbon source at a temperature of 700 °C [11]. First, the furnace was heated at 15 °C min^{-1} to 750 °C in a flow of 800 sccm Ar and 200 sccm H_2. At 700 °C, 100 sccm of C_2H_4 was added for 5 min, and then the furnace cooled at 15 °C min^{-1} in 1000 sccm Ar. The production methods for catalytically grown nanotubes are now well established and allow synthesis on a scale of grams per day.

The membrane used in this work was Nafion® 117 (DuPont, E.W. = 1100). The Pt/SPE composite was prepared by a chemical plating method, which is similar to that reported in previous papers [12–15]. The Nafion® membrane pretreatment involved the following steps. First, roughening of the membrane surface was achieved with abrasive paper. Then, the membrane was subject to treatment to remove organic and metallic impurities, including heating the membrane in 3 mass % H_2O_2 to about 70 °C for 1 h to remove organic impurities, then in 1 M H_2SO_4 solution at 80 °C for 40 min to remove metallic impurities. Thereafter, the membrane was swollen in deionized water for 30 min at 130 °C under elevated pressure. Finally, the membrane was boiled in pure water several times. These conditions were identified as optimal to obtain surface-specific membrane resistance.

The pretreated membrane was mounted in a two-chamber cell. One compartment was filled with 0.05 M H_2PtCl_6 solution, the other with an aqueous solution of 3 mass % hydrazine. The reducing agent diffused across the membrane and reduced the metal-complex ion in close proximity to the membrane surface. The result platinum layer was fixed to the membrane surface. Plating on the other side of the membrane was achieved by turning the membrane around.

2.2. *Purification procedure*

Figure 1 shows a plane schematic diagram of the typical SPE electrolysis cell in our laboratory for anode oxidation of carbon nanotubes. In each procedure, 50 mg of nanotube soot was added to 200 mL pure water. After pouring the suspension into the anode chamber, the raw materials were purified by anodic oxidation at 150 mA cm^{-2} and 12 V, 80 °C for 3 h. In the electrolysis process, pure water was gradually added to the cell to compensate the consumption of water during the electrolysis. The resultant dispersion was then centrifuged to obtain a precipitate rich in carbon nanotubes. The purified sample was purged only twice with high purity deionized water and dried.

2.3. *Evaluation*

The effectiveness of the above procedure for purifying CNTs was evaluated by transmission electron microscopy (TEM) observations, a thermogravimetry (TG), differential thermal analysis (DTA) and Raman spectra.

The morphology of raw materials and purified CNTs was observed by TEM (JEM–100 CX II, 80 kV). The CNTs before and after purification were heated in a thermobalance (BeiF WCT-1) at a programmed rate of 10 °C min^{-1} in air atmosphere. TG–DTA graphs were plotted using a RSZ thermoanalysis system. Raman spectra of the CNT from 600 to 2000 cm^{-1} before and after purification with a laser wavelength of 514.5 nm (slit width 25 μm) were obtained from a Renishaw System RM–1000.

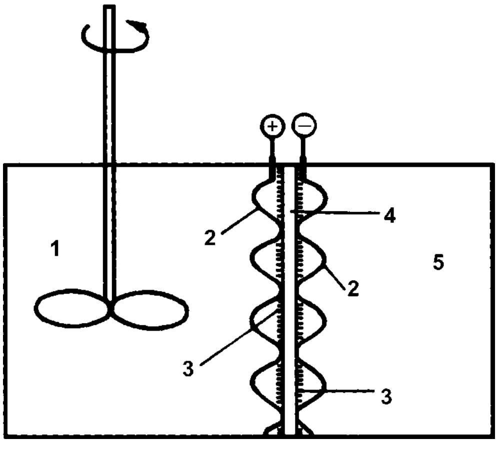

Fig. 1. A plane schematic diagram of the typical SPE electrolysis cell. Key: (1) anode chamber, (2) current collector, (3) catalyst layer, (4) Nafion® 117 and (5) cathode chamber.

3. Result and discussion

After purification, most of the carbonaceous impurities are removed without significant damage to the bundles and transition-metal catalyst particles adhered to the inner wall of tubes remained. This is based on the following TEM observations. For multiwalled tubes, the tube wall and cavity should be easily distinguished if the tube surface is clean. But the TEM picture of raw materials (Figure 2(a)) shows a vague feature. This means that they had absorbed a lot of carbonaceous impurities on their surface. From Figure 2(b), the tube of purified sample is thinner and the wall-cavity is much clearer. It is likely that most of the tube-attached carbonaceous impurities are removed. These are the major impurities for carbon nanotubes prepared by our process. The removal of this kind of impurity is the most difficult part of the purification process, because it is generally accompanied by damage of the tube wall during the oxidation processes. For example, the tubes will be broken and become shorter by HNO_3 oxidation. But after anodic oxidation, the tubes maintain a long chain, which is very important for the mechanic

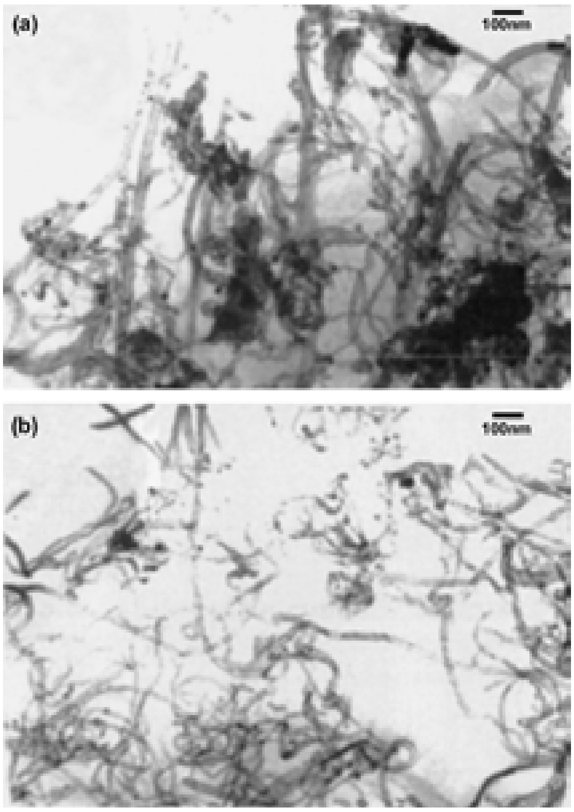

Fig. 2. TEM images of (a) a raw nanotube sample synthesized in a tube furnace with a Ni-catalyst where ethylene gas was used as a carbon source at a temperature of 700 °C; and (b) a purified carbon nanotube sample prepared by anodic oxidation in a SPE cell.

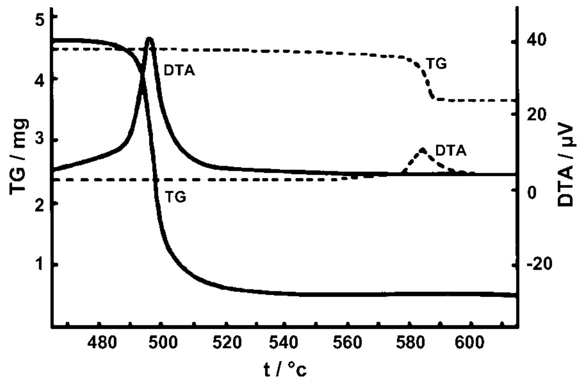

Fig. 3. Thermogravimetric and differential thermal analyses of raw materials (solid line) and purified nanotubes (dashed line) at a heating rate of 10 °C min^{-1} in air. The TG–DTA graphs were plotted using a RSZ thermoanalysis system.

reinforcement application of the tubes [11]. However, some transition-metal catalysts inside the tube can still be seen.

In each thermal analysis experiment, about 4.5 mg of raw materials or purified samples was heated from room temperature (25 °C) to 650 °C, then maintained at 650 °C for 150 min. According to Pang et al. [16], carbon nanotubes are more resistant to oxidation than other forms of carbon. Under the conditions (at 650 °C for 150 min in air), carbonaceous impurities will be gasified (presumably as CO and/or CO_2) by oxidation. In TG for raw materials (solid line in Figure 3), the maximum rate of weight loss took place at 496 °C, while for purified materials (dashed line in Figure 3) at 586 °C. This is the first time that DTA has been used to study CNTs. From the position and area of the sample's exothermal peak, we can estimate the temperature range and the ratio of carbonaceous impurity. Obviously, the position of the exothermic peaks in the DTA graph is consistent with that of the inflection point in the TG graph. The peak area of raw materials is much larger than that of purified materials, which also supports that the purified sample has a high purity.

Figure 4 shows Raman spectra of the CNT from 600 to 2000 cm^{-1} before and after purification. Nanotubes have distinctly different Raman peaks from other carbonaceous materials [17–19], that is, CNTs show characteristic peaks centred at about 1500 $\sim$ 1600 cm^{-1} (G line) as their cylindrical symmetry. Amorphous carbon or carbonaceous nanoparticles generally show a broad peak near 1350 cm^{-1} (D line). Their relative intensities provide a purity indication. Compared with the Raman Spectrum of raw material (Figure 4(a)), the material after purification shows low impurity content, as the spectrum (Figure 4(b)) has lower ratio between the D and G line intensity. However, the peak around 1340 cm^{-1} did not disappear after purification. This situation also appeared in the HNO_3 oxidation process. Duesberg [20] and Holzinger [21] suggested that the existence of the 1340 cm^{-1} peak after oxidation might originate from disordered or carboxylated carbon, which is formed on oxidation.

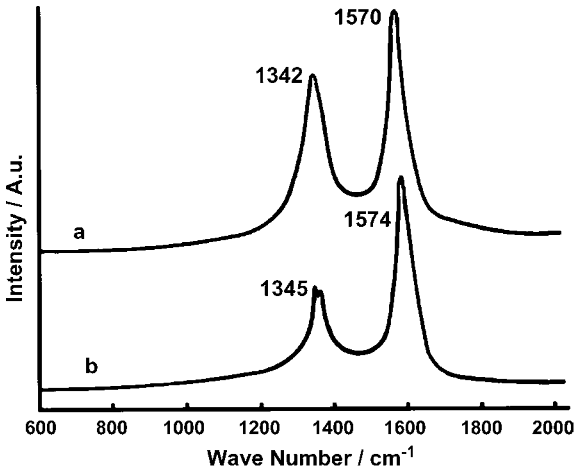

Fig. 4. Raman spectra of the CNT from 600 to 2000 cm^{-1} before and after purification with a laser wavelength of 514.5 nm (slit width 25 μm). The spectra were obtained from a Renishaw System RM–1000: (a) raw materials, (b) purified CNTs.

4. Conclusion

A new technique for purifying carbon nanotubes utilizing anodic oxidation in a SPE cell has been developed. On the basis of TEM observations, TG–DTA graphs and Raman analyses, it is found that most of the carbonaceous impurities are removed from the roots without significant damage to the bundles. SPE electrolysis can be carried out in pure water, compared with the widely used HNO_3 oxidation process, this process demands less subsequent washing and separation steps.

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