Freestanding bucky paper with high strength from multi-wall carbon nanotubes

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HIGHLIGHTS

- Multi-wall carbon nanotube bucky paper.
- Structural defects of carbon nanotubes.
- CoMo catalyst.
- Tensile strength of bucky paper.

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ABSTRACT

Bucky papers have been investigated by some research groups, however, due to different qualities of carbon nanotubes used, various results of strength and electronic properties were reported in the literatures. In this article, the effects of carbon nanotubes synthesized over different catalysts on the qualities of bucky papers were systemically investigated. Multi-wall carbon nanotubes were synthesized over a series of MgO supported catalysts with different weight ratios of Mo and Co. As the ratios of Mo/Co in the catalysts were increased from 0 to 3, the yields of carbon nanotubes were enhanced from 7 wt% to 400 wt%. However, the yield enhancement of carbon nanotubes was achieved at the expense of higher proportion of structural defects within carbon nanotubes, which has been proved by Raman spectrosopy and thermogravimetry analysis. It was demonstrated that the tensile strength of bucky paper composed of numerous MCNTs bundles strongly depends on the structure of carbon nanotubes used. By optimizing reaction conditions, a bucky paper with high strain up to 15.36 MPa and electrical conductivity of 61.17 S cm\textsuperscript{-1} was obtained by Supercritical Fluid (SCF) drying technique.

1. Introduction

Bucky paper is a kind of carbon nanotube film prepared by the filtration of carbon nanotubes (CNTs) on porous membrane, such as highly ordered anodic aluminum oxide (AAO), PTFE and polycarbonate. Those bucky papers have unique properties in electrical conductivity, field emission properties, gas permeability and mechanical properties [1–5] due to the distinctive structure of carbon nanotubes [6–8].

Bucky papers reported so far were usually made from single-wall carbon nanotubes (SCNTs) or double-wall carbon nanotubes (DCNTs) [9–12]. Endo et al. [9] investigated the preparation of bucky paper using SCNTs and DCNTs with different surface areas and microvolumes. Moreover, they reported that the purity of SCNTs played a key role to achieve high quality of bucky paper. Very small amount of impurities in SCNTs, such as catalyst particles encapsulated in graphitic carbon, will lead to a poor mechanical strength of the paper and result in a very brittle bucky paper obtained. Kumar et al. [12] studied the effect of nitric acid oxidation on the stability of SCNTs with a mean diameter of around 1 nm. It was found that SCNTs with small diameters were easily destroyed in high concentration HNO\textsubscript{3} of 10 M, the tensile strength of bucky paper is increased from 10 to 74 MPa after experiencing the high concentration of nitric acid solution treatment, indicating that increasing the diameters of SCNTs lead to higher tensile strength of bucky paper. However, this is only for the case of bucky paper made from single and double-walled carbon nanotubes, while multi-wall carbon nanotubes with high purity have larger diameter ranging...
from 10 to 100 nm compared to SCNTs and DWNTs with smaller diameters ranging from 0.4 to 3 nm [8,13–17]. In contrast to the synthesis of SCNTs and DCNTs, the preparation of MCNTs is easier using chemical vapor deposition (CVD) method. but little is known about the effect of catalyst composition on the structure of MCNTs as well as the relationship between the structure of MCNTs and the quality of bucky paper formed. MCNTs-based bucky paper has been synthesized by a quick frit compression method, however, small sized paper with a diameter of 1.5 cm was obtained [18]. Zeng et al. [19] prepared MCNTs bucky paper modified by vanadium oxide. It is reported that composite bucky paper used as capacitor showed high capacity.

In this paper, the effect of catalyst composition on the yield and structure of carbon nanotubes was thoroughly investigated, and the mechanical strength of freestanding bucky papers prepared from different MCNTs was compared. The Mo/Co ratios of catalysts have great effects on the yield and the quality of MCNT. High yield from different MCNTs was compared. The Mo/Co ratios of catalysts at the expense of more structural defects being introduced. For the first time, we demonstrated that high tensile strength was obtained from the bucky paper made from these less defects MCNTs.

2. Experimental

2.1. Preparation of catalyst and carbon nanotubes

CNTs were produced by chemical vapor deposition (CVD) of methane over MgO supported Co and Mo catalysts as described elsewhere [20]. The cobalt and molybdenum on magnesium oxide was prepared by impregnating MgO with the aqueous solution of Co(NO$_3$)$_2$·6H$_2$O and (NH$_4$)$_2$Mo$_6$O$_{24}$·2H$_2$O. The cobalt loading in the catalyst was fixed at 4 wt% for all catalysts. The molybdenum loading in the catalyst was varied by different Mo/Co ratios from 0 to 3. Typically, 0.5 g of the catalyst was put into a quartz tube in a tube furnace. The catalyst powder was first reduced by heating at 800 °C in 10% H$_2$/Ar at a flow rate of 200 ml min$^{-1}$ for 30 min, methane was then passed through the catalyst powder at a flow rate of 200 ml min$^{-1}$. After the reaction, the furnace was cooled down to room temperature under Ar flow.

The yield of deposited carbon is calculated as the following:

$$\% \text{ Carbon yield} = \frac{(W_f - W_c)}{W_c} \times 100$$

where $W_c$ is the initial weight of catalyst, $W_f$ the total weight of the sample gathered from the reactor. To purify CNTs, the as-prepared catalyst/carbon mixture was treated with 3 M HNO$_3$ for 6 h and washed by distilled water to remove the catalyst.

2.2. Preparation of bucky paper

Prior to the preparation of bucky paper, the surface of CNTs is functionalized according to following procedure. 1.0 g of purified CNTs was mixed with high concentrated acid (HNO$_3$/H$_2$SO$_4$ = 1/3) and refluxed for 4 h. After that, the mixture was turned into a homogeneous, black suspension. Upon the centrifugation of 11,000 rpm for 20 min, the suspension separated into black carbons precipitate and a light-brown supernatant, then upper layer acid solution was removed to leave the acidified precipitate. The precipitate was washed with water till pH neutral and dispersed in distilled water. The CNT suspension was then filtered using a polycarbonate membrane with the pore size of 0.2 μm to make a wet bucky paper.

The dried bucky paper was then obtained by Supercritical Fluid (SCF) drying technique. Typically, a wet bucky paper was placed into a stainless steel cell, then the cell was filled with CO$_2$ and maintained at 1500 psi in a 40 °C water bath for 30 min [21]. After CO$_2$ and water moisture was released, the dried bucky paper was obtained.

2.3. Characterization of carbon nanotubes and bucky paper

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6700F at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was conducted on a JEOL 100EX operating at 100 kV. Samples for TEM analysis were prepared by dispersing CNT powder in ethanol and deposited onto Ni grids. Raman spectra were recorded on a Renishaw 1000 Raman system in an ambient atmosphere using a 5 mW He–Ne laser ($\lambda = 514.5$ nm) and a CCD detector. Thermal gravimetric analysis (TGA) of the CNT samples was performed at a heating rate of 10 °C min$^{-1}$ up to 800 °C in air flow of 75 ml min$^{-1}$. The tensile mechanical properties of CNTs films were determined using INSTRON 5565. Tensile tests were conducted on specimens with 12.0 mm wide at a gauge length of 10 mm and a strain rate of 10 mm min$^{-1}$. The resistivity of the bucky paper was measured by the standard programmable DC voltage/current detector four-point probe method. The bucky paper were cut with the size of 10 mm × 10 mm, each data presented is the average value of the measurements from three tested samples. The electrical conductivity of the bucky paper was calculated based on the equation as following:

$$\rho = \frac{KV}{I}$$

where $\rho$ is the bucky paper’s electrical conductivity in S cm$^{-1}$, $K$ is geometry factor of 2.2, which is determined by using copper film (11 mm × 11 mm × 200 nm) as reference (resistivity of copper film is 17.2 μΩ m). $V$ is the voltage in mV, $I$ is the current in mA, $t$ is the film thickness measured by a digital micrometer in μm.

3. Results and discussion

3.1. Influence of catalysts on the carbon yield

In all experiments, the weight of catalyst is kept at 0.5 g, the carbon yields of samples synthesized on catalysts with different Mo/Co ratios are shown in Fig. 1. The carbon yield is calculated gravimetrically compared to the initial weight of catalyst used. It is found that only 7 wt% carbon yield is obtained on a 4 wt% Co/MgO

![Fig. 1. Carbon yields on supported catalysts with different Mo/Co weight ratios.](image-url)
catalyst at 800 °C, which is about 10 times lower than that on a catalyst with Mo/Co ratio of 0.75. Also, yields of carbon nanotubes are extremely high, up to 254 wt% and 302 wt%, relative to the weight of catalyst as Mo/Co ratio in the catalyst is increased to 1.5 and 2. Moreover, the carbon yield of the sample prepared on a catalyst with a Mo/Co ratio of 3 is as high as 400 wt% compared to the initial weight of catalyst used. This is the highest carbon yield achieved so far using this type of catalyst though it is well known that high Mo additive in the catalyst usually result in high yield of carbon yield [22,23]. In our experiments, developed catalysts can work as long as 120 min. For example, a catalyst of Mo/Co ratio of 1.5 generate about 204 wt% carbon yield at the reaction time of 90 min, while the carbon yield is increased to 254 wt% when the reaction time is prolonged to 120 min, which suggests that high yield of MCNTs considerably depends on a highly active catalyst.

3.2. Characterization of CNTs

Detailed observation in TEM presented in Fig. 2 suggested that carbon nanotubes are formed on all catalysts. The mixture of SCNTs and MCNTs is produced on a 4 wt% Co/MgO catalyst and a catalyst with Mo/Co ratio of 0.75, while only MCNTs are generated when using catalysts with Mo/Co ratio of larger than 1.5. Thus, in order to investigate the effect of purified multi-wall carbon nanotubes on the quality of bucky paper, three MCNTs generated on the catalysts with Mo/Co ratio between 1.5 and 3 are compared.

Raman spectra and TG analysis are used to characterize the structure and graphitization degree of CNTs synthesized on the catalysts with different Mo/Co ratios. The Raman spectra of MCNTs in Fig. 3 display strong G-band at 1575 cm\(^{-1}\) and weak D band at 1320 cm\(^{-1}\). The band located at approximately 1320 cm\(^{-1}\) is attributed to defects in graphene layers and lattice distortions in the carbon structures. The band at about 1575 cm\(^{-1}\) is G-band, which is characteristic of perfect graphite [24]. In comparison, the relative intensity of the G-band of MCNTs is stronger than that of the D-band for all three samples. However, intensity ratios \(I_G/I_D\) of MCNTs prepared on catalysts with Mo/Co ratio of 1.5, 2 and 3 are 5.77, 1.70 and 1.18, respectively. The maximum intensity ratio \(I_G/I_D\) of MCNTs is achieved on the catalyst with Mo/Co ratio of 1.5 and the intensity ratio between the G-band and D-band \(I_G/I_D\) is decreased with the increase of Mo/Co ratio, indicating that less defects and higher graphite degree on the structure are present on MCNTs prepared over the catalyst with lower Mo/Co ratio.

Fig. 4 shows the TGA data measured for MCNTs prepared on catalysts at 800 °C. The weight loss of the sample in air occurs at about 470 °C and continues to about 620 °C for three MCNTs.

**Fig. 2.** TEM images of MCNTs prepared at 850 °C on supported catalysts with different Mo/Co weight ratios of (a) 0, (b) 0.75, (c) 1.5, (d) 2, and (e) 3.
found that an increase in temperature of 40 °C is observed on MCNTs prepared on a catalyst with Mo/Co ratio of 1.5 when compared with two curves of carbons prepared on the catalyst with Mo/Co ratio of 2 and 3, indicating that higher crystalline structure of MCNTs is obtained from this type of catalyst. TG results also show that the residues of three MCNTs prepared on the catalysts with Mo/Co ratios of 1.5, 2 and 3 are 1.17 wt%, 1.09 wt% and 1.75 wt%, respectively. These residues might be catalyst nanoparticles encapsulated by carbon layers, which were not completely removed by nitric acid treatment [25].

3.3. Mechanical and electrical properties of bucky paper

In order to make homogenous CNTs solution for the preparation of bucky paper, MCNTs was first oxidized using a mixed acid. The treatment step of CNTs refluxed in a high concentrated HNO3/H2SO4 solution is to create functional groups such as OH, COOH on the surface of CNTs [26]. It is worth to note that MCNTs without refluxing with mixed acid could not form a complete film after the filtration, only split spots were found on the PC film after drying. The refluxed temperature of synthesized carbons in mixed acid is optimized at 120 °C, oxidative treatment of carbon nanotubes at high temperature than 140 °C results in larger amount loss of carbon nanotubes, due to the destroy of carbon nanotubes. More amorphous carbons deposited on the surface of CNTs are observed in TEM if refluxed temperature of solution is close to 140 °C, as shown in Fig. 5, and only about 20 wt% carbons are left after the centrifugation. Previous studies indicates that oxidation treatment is a necessary step for the generation of large quantity groups on the surface of carbon although some defects are also created, which has been demonstrated to have a strong tendency to stick together [27].

The digital camera images of bucky papers prepared by MCNTs on catalysts with Mo/Co ratio of 1.5, 2 and 3 are shown in Fig. 6. The freestanding, well shaped bucky paper with a diameter of 3.7 cm can be made using carbons prepared on a catalyst with Mo/Co ratio of 1.5, the bucky paper is very flexible and easy to be bended to various shapes after Supercritical Fluid (SCF) drying, as shown in Fig. 6a and b. In contrast, an incomplete, freestanding bucky paper is made by MCNTs prepared a catalyst using a Mo/Co ratio of 2, the edge is damaged when bucky paper was peeled off from the PC substrate using a tweezers, as shown in Fig. 6c. Although bucky paper is somewhat brittle compare to that in Fig. 6a, The paper still could be folded to some shapes. However, a split bucky paper is
Fig. 6. Digital camera images of freestanding bucky papers with MCNTs prepared on the catalysts with Mo/Co ratios of (a) and (b) 1.5, (c) 2, (d) 3.

Fig. 7. SEM images of bucky papers of carbons prepared on the catalyst with Mo/Co ratios of (a) and (b) 1.5, (c) and (d) 2.
obtained when using MCNTs prepared on a catalyst with Mo/Co ratio of 3 in Fig. 6d. These bucky paper pieces are very brittle and easier to break down.

SEM micrographs in Figs. 7 and 8 show the surface and cross section morphology of bucky paper composed of interconnected MCNTs. The bucky papers prepared by MCNT synthesized on catalysts with Mo/Co ratio of 1.5 and 2 are composed of bundles of MCNTs physical entangled together, as shown in Fig. 7a and c. The cross-sections of SEM images of bucky paper of MCNTs shows that the thickness of bucky paper are about 30 μm in Fig. 7b and d. However, lots of MCNTs are protruding out of the surface of bucky paper in Fig. 8a when using MCNTs prepared on a catalyst with a high Mo/Co ratio of 3.

The mechanical properties of freestanding bucky papers are shown in Fig. 9. It is difficult to measure the strength of bucky paper of MCNTs prepared on a catalyst with Mo/Co ratio of 3 due to its brittleness nature, thus only two bucky papers of MCNTs prepared on catalysts with Mo/Co ratio of 1.5 and 2 are compared. Two bucky papers of MCNTs exhibit plastic behavior before they break. The tensile measurement of bucky paper of MCNT prepared on a catalyst with Mo/Co ratio of 1.5 showed that the tensile strength to break value is about 15.36 MPa, five times stronger than that of MCNT bucky paper of 2.77 MPa prepared on a catalyst with Mo/Co ratio of 2.

As the bucky papers were prepared under the same procedure including acid concentration, treatment temperature and reaction time, however, different results are obtained. Therefore, it is believed that the only difference in the quality of bucky paper is attributed to synthesized MCNTs with different structure and graphite degree. Highly active catalyst with high Mo/Co ratio can generate larger quantity of CNTs, but more structural defects are present in the CNTs, which lead to poor mechanical property. The effects of defects within single SCNT on the mechanical property have been predicted by simulation calculations [28,29]. In this paper, we demonstrated that the tensile strength of bucky paper composed of numerous MCNTs bundles also strongly depends on the structure of carbon nanotubes used.

In order to further investigate potential application of bucky paper as electrical device, we selected a bucky paper with best tensile property to measure its electrical properties. The measurement was repeated 6 times using different pieces of bucky paper, and the results are shown in Table 1. The bucky paper thickness is about 34 μm measured by a digital micrometer, which is similar to that obtained by SEM. The free standing bucky paper exhibits an average resistivity of 0.01641 U cm and average conductivity of 60.9599 S cm⁻¹, indicating that freestanding film has potential application for electrode material.

### 4. Conclusion

MCNTs were prepared on the catalysts with different Mo/Co ratios. The yields and structure of CNTs are considerable dependent on the Mo additive amount within catalyst used. Carbon nanotubes yields are increased from 254 wt% to 400 wt% on the catalysts with the increase of Mo/Co ratios from 1.5 to 3. However, the quality of

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CNTs decreased when using the catalyst with high Mo/Co ratios. The structure and graphite degree of MCNTs may play key role for high quality of bucky paper. The high quality bucky paper with high strain up to 15.36 MPa and conductivity of $61.17 \text{ S cm}^{-1}$ was synthesized by carbons prepared on a catalyst with Mo/Co ratio of 1.5.

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