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Structural modification of carbon nanotubes by various ball milling

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Abstract

Shortening and opening of chemical vapour deposition (CVD)-processed multi-wall carbon nanotubes (MWCNTs) were examined using various ball milling methods. Dry ball milling resulted in a rapid collapse of nanotubes, while wet milling with alcohol was effective to get short and open-tip nanotubes. The shortened and open MWCNTs by wet milling were filled with nanoparticles by capillary infiltration and a subsequent heat treatment. The structurally modified MWCNTs by shortening, opening and filling exhibited improved Li-storage properties.

Keywords: Nanostructured materials; Mechanical alloying; Vapour deposition; Electrode materials; Energy storage materials

1. Introduction

Carbon nanotubes (CNTs) have shown promising potential for application in many engineering fields due to their many unusual properties. For some electronic or structural applications, long CNTs are required to be used as strong and conducting nanocables. The catalytic chemical vapour deposition (CCVD) process, which is simple and the most practical method for mass production, usually generates long CNTs. The CCVD-processed CNTs are often in the form of tangled agglomerates consisting of individual nanotubes with lengths ranging from 100 mm to several millimetres. The longest CNTs reported so far have lengths up to several tens centimetres [1,2]. However, for many other applications such as chemical or energy-storage use, it is desirable to have short nanotubes with open tips to facilitate diffusion and chemical reactions [3–5]. The closed tip of as-synthesized nanotubes hinders atomic or ionic diffusion into the tube interior. Open-tip structure makes the interior accessible for various atoms and molecules. In order to increase the number of active sites one has to cut the tubes into pieces. The short and open CNTs are also beneficial to exploit their high modulus and strength in composite applications because of difficulties in their uniform dispersion in the matrix phase. Thus, one of the important challenges in application for CNTs lies in shortening and opening of CNTs to attain novel mechanical, chemical and transport properties.

Several methods have been attempted to get short and open-ended CNTs: acid etching [6,7], ultrasonic treatment [8] scanning tunnelling microscope (STM) voltage [9], radiation treatment [10] and ball milling [11–16]. Among them, ball milling seems to be the simplest process for cutting CNTs. Ball milling is a good method to crack and to open the closed ends of CNTs. However, it is often ineffective to cut CNTs taking very long time (>100 h) [14,15], and needs abrasive milling additives such as diamond [11] or oxide powders [13]. Some worker have used organic materials such as cyclodextrin or polycarbonate for encapsulation of CNTs before milling [17,18]. The disadvantage of these methods using additives or encapsulation is that it would be difficult to separate CNTs from the additives after ball milling.

In the present work, we have thoroughly examined ball-milling process to shorten and open CCVD-processed multi-wall carbon nanotubes (MWCNTs). Different ball-milling methods were employed: dry milling in air or in ammonia, wet milling in ethanol or in water, dry milling of polycarbonate-encapsulated CNTs, dry milling with additives. To demonstrate the advantageous aspect of the structurally modified CNTs, the shortened and opened nanotubes were filled with nanoparticles and their resulting properties of lithium intercalation are examined.

2. Experimental

The MWCNTs were synthesized by catalytic CVD method at 600–900 °C for 20 min in a quartz tube using acetylene gas as a carbon source. Ferrocene was used as a catalytic precursor. By a proper control of processing parameters,

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MWCNTs with two different morphologies were synthesized and used as starting powders: entangled aggregates and well-aligned bundles.

To cut and open MWCNTs, several milling methods were employed: dry milling in air or in ammonia, wet milling in ethanol or in water, dry milling after PC (polycarbonate)-encapsulation, dry milling with additives (10 wt.% Fe or Fe_2O_3 powder). For PC-encapsulation, MWCNT were dispersed in PC containing chloroform solution, followed by drying. After ball milling, PC was removed by washing with chloroform. All ball-milling process was carried out in a planetary mill using 300 ml using a stainless steel vial and 6 mm diameter steel balls. The rotating speed of the vial was 200 rpm and the ball-to-powder weight ratio was 50–500:1. After ball milling, MWCNs were purified by ultra-sonication in a 3:1 (v/v) mixture of concentrated H_2SO_4 and HNO_3 at 30–140 °C for 10 h, followed by centrifugation, repeated washing with water until pH ~7 and drying.

Li-storage property of the structurally modified MWCNTs were evaluated by charge–discharge test using nanotube powder as anode materials in Li-ion cells. The electrodes were made by dispersing 95 wt.% MWCNT and 5 wt.% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry, which was then spread onto a copper foil. The cell was assembled in an argon glove box using Li as a counter electrode. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The cells were galvanostatically charged and discharged at a current density of 20 mA/g over the voltage range 0.01–2.5 V versus Li/Li^+.

3. Results and discussion

The MWCNTs used in this ball milling study have two different morphologies, entangled and straight ones. Both materials have closed tips, a length of several hundreds microns and an outer diameter of 15–30 nm (8–20 walls) with relatively small inner diameters (3–8 nm).

During dry ball milling, MWNTs tended to be compacted by the balls and form large agglomerates. The aggregates formed by flattening of nanotubes even after dry milling for 1/2 h, showing multi-layered carbon structures (Fig. 1a). After 10 h, the nanotubes near the edge of the agglomerates became very smooth (Fig. 1b). This indicates that the broken and sharp tips of nanotubes produced by ball milling become closed to reduce their high surface energy. The closing of tips was confirmed by TEM (Fig. 4a). After 30 h, individual nanotubes collapsed completely forming round shaped particles (Fig. 1c and d). High resolution TEM showed that most of the multi-layered graphite structure persists with partly amorphous regions. By radial deformation produced by ball milling, the inner nanohole structure gradually collapsed to a usual layered structure of graphite by the inter-sheet attraction between opposite sides of the inner wall when the agglomerates of multi-layered carbon structure formed. The structural development during the dry milling was similar both in milling in air and in an ammonia atmosphere. Dry ball milling with additives (10 wt.% Fe or Fe_2O_3 powder) reduced to some extent agglomeration, but the elimination of these additives after ball milling was difficult.

Wet ball milling produced a quite different result. The MWCNTs with new tips generated and the length decreased gradually (Fig. 2a and b). No apparent collapse of nanotube structure was observed even after 150 h. This is attributed to the presence of liquid phase which might alter van der Waals interaction between nanotubes, preventing them from adhering. Another possibility

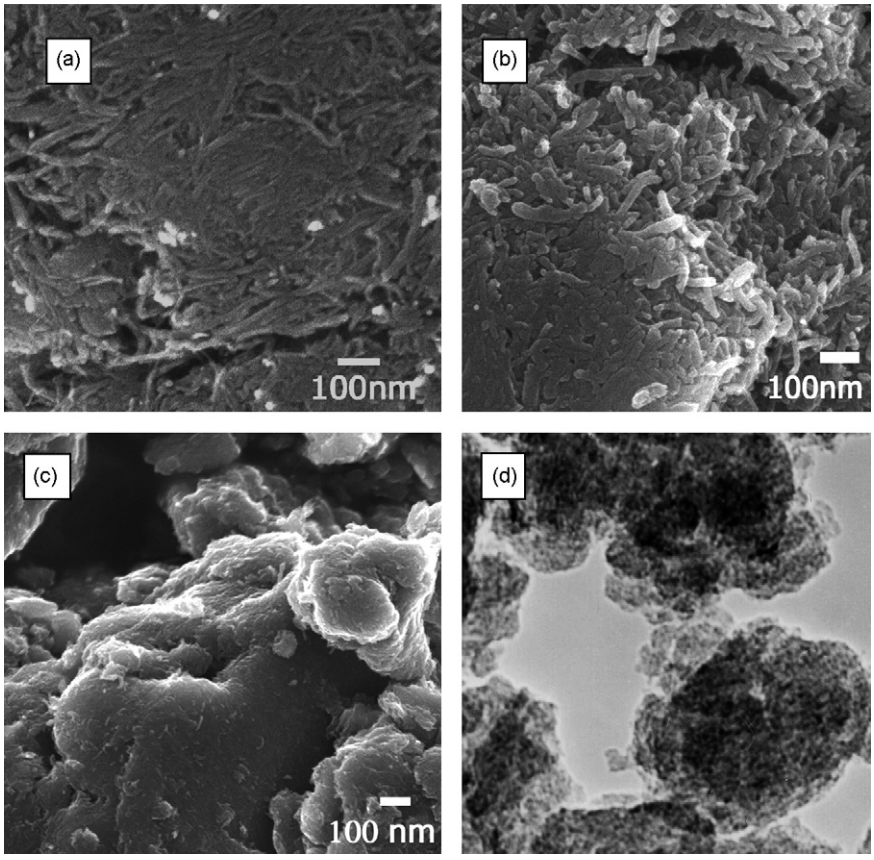

Fig. 1. Morphology of dry milled MWCNTs: FE-SEM images after 1/2 h (a), 10 h (b), and 30 h (c), and TEM image after 30 h (d) (secondary electron images).

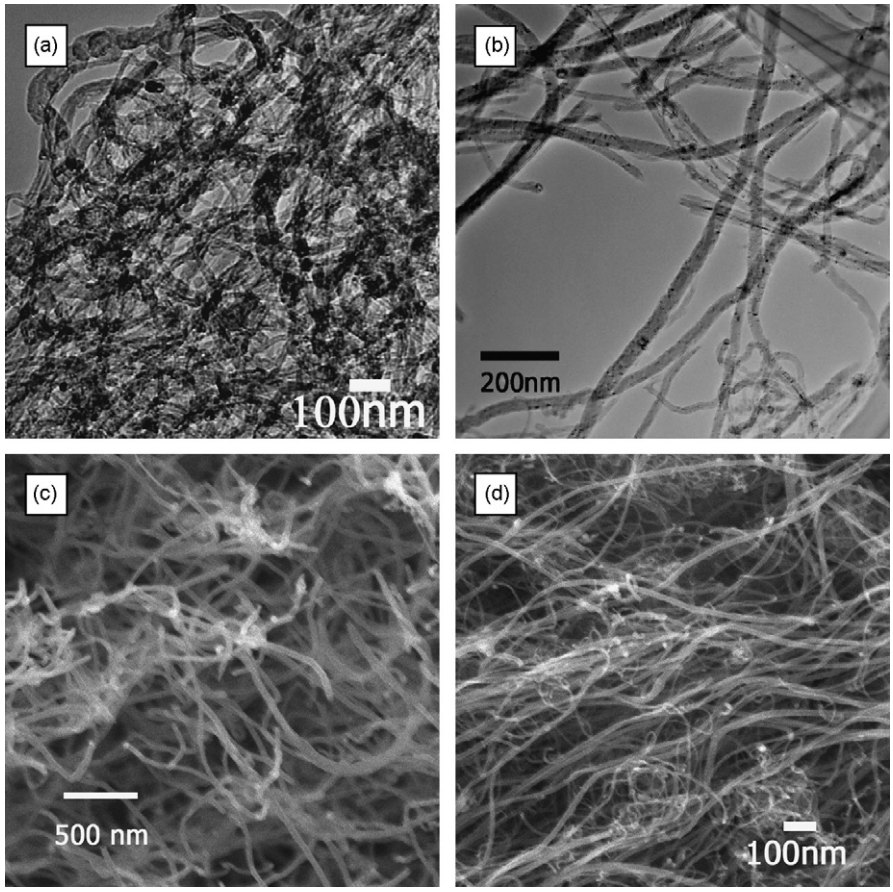

Fig. 2. Morphology of wet milled MWCNTs (wet milling in water): TEM images after 0 h (a) and 10 h (b), and FE-SEM images after 30 h with starting nanotubes of entangled (c) and straight form (d) (bright field images).

is that many surface polar groups existing on the surface of nanotubes such as C–O, C=O and O–C=O [18] combine with ethanol through the strong intermolecular interaction, resulting in local weakening and hence cutting of nanotubes. In fact, cutting was more effective in wet milling with carbon-containing ethanol than in milling with water. The cleavage of the nanotubes occurs at defect sites such as nanotube kinks which can be originated from the stresses induced by the milling. Curved nanotubes contain many structural defects such as pentagon and heptagon carbon bond. As a result, the starting nanotubes with entangled form were much better shortened than those with straight form (Fig. 2c and d).

XRD results confirm the observations shown above. For dry ball milling, the major peaks (0 0 2) became slightly pronounced with increasing milling time, indicating gradual development of multi-layered graphene layers during ball milling (Fig. 3a).

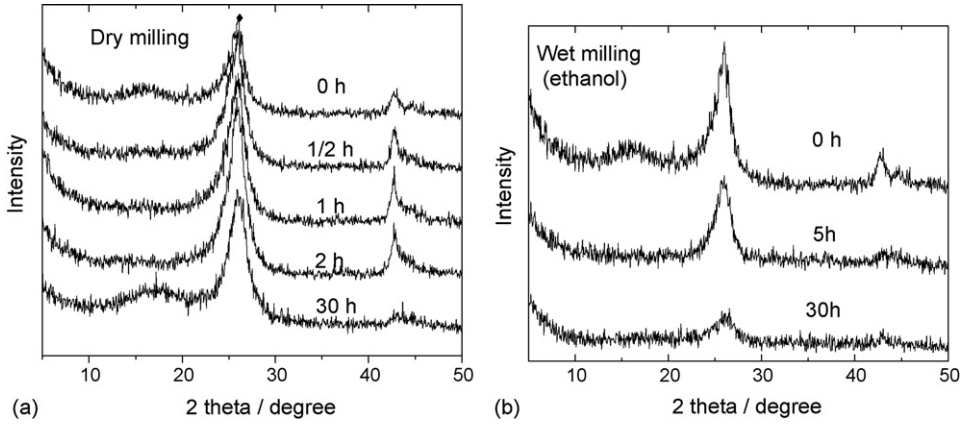

Fig. 3. Change in XRD patterns with milling time: dry milling (a) and wet milling with ethanol (b).

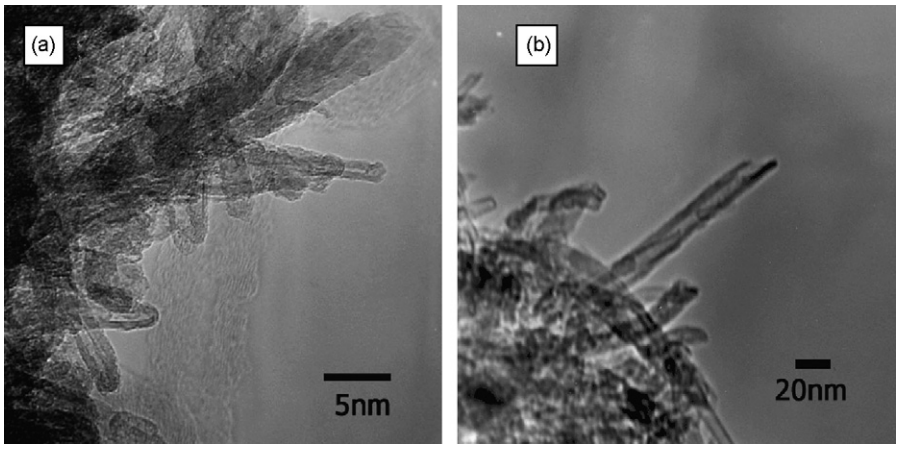

Fig. 4. TEM micrographs showing CNT tips: dry ball milled (a) and wet ball milled (b) for 10 h (bright field images).

After dry ball milling for 30 h, a partial amophization and/or disordering started with broadened peaks near $2\theta = 10–20^\circ$. On the other hand for wet ball milling, the (0 0 2) peaks weakened with time because of weakened carbon multi-layer structures by shortening and isotropic distribution of nanotubes (Fig. 3b).

Another important feature showing the difference between dry-milled and wet-milled MWCNTs is their tip. The tips of dry-milled nanotubes are mostly closed (Fig. 4a), while those of the wet-milled ones are mainly open. Nanotubes are considered metastable compared to conventional graphite due to strain energy [19]. Therefore, the broken and opened nanotubes by dry ball milling tend to close their tips by taking round edge shape to minimize energy. For wet milling, on the other hand, strain energy can be sufficiently reduced by adsorption or intermolecular attraction between the nanotubes and the liquid phase.

Such open structured is very important for further filling of nanotubes with exotic substances. An example is given in Fig. 5. Both dry and wet milled MWCNTs were impregnated in a $SnCl_2$ dissolved HCl solution. After the impregnation by capillary action, the nanotubes were dried and heated at 600 °C to form SnO_2. For the slightly dry milled MWCNTs with closed tip, SnO_2 nanoparticles cover the surface of nanotubes, but they are almost invisible inside core holes. For the wet milled and open MWCNTs, on the other hand, nanosized SnO_2 penetrated into the tube core.

To demonstrate the possible use of the nanoparticle-infiltrated CNTs, we have examined Li-storage properties of the above materials (Fig. 6). As an anode material for Li-ion batteries, SnO_2 is a good candidate to replace conventional graphite. In spite of high capacity at the first cycle, its capacity degrades rapidly upon repeated cycling (Fig. 6b) because of electrode disintegration by volume expansion. As-synthesized carbon nanotubes, on the other hand, have closed tips and a much bigger inner tube diameter for lithium ions to be hosted inside. Nanosized SnO_2-filled CNTs can thus offer many advantages over nanotubes and SnO_2. For SnO_2 the problem of the volume expansion could be minimized in such confined space inside tube hole. For CNTs moderately filled tube structure could readily host and store lithium ions. Although we could not fully optimized the processing and the related filling structure, the preliminary result showed the nanosized SnO_2-filled CNTs exhibit high capacities combined with stable cycle properties after the first cycle.

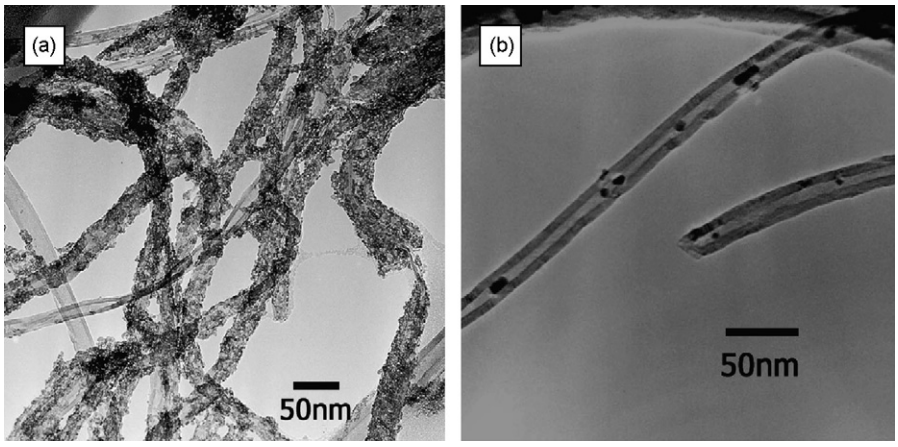

Fig. 5. Nano-SnO_2-treated MWCNTs with dry milled CNTs (a) and wet milled CNTs (b) (bright field images).

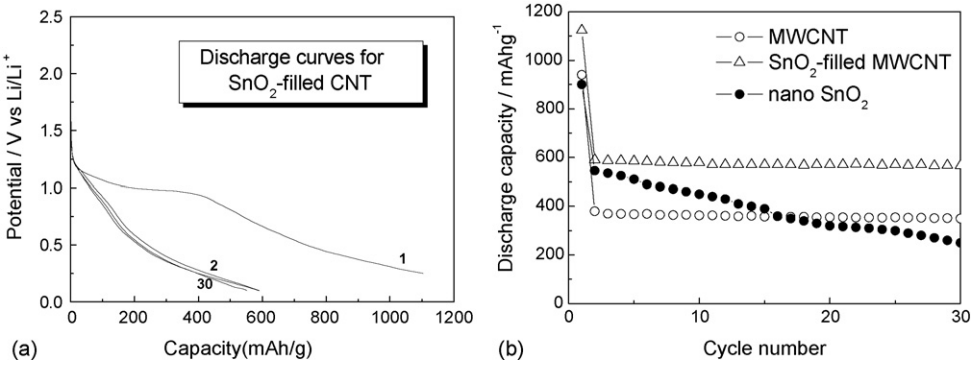

Fig. 6. Li-storage capacity of as-synthesized MWCNT, nano-SnO_2, and nano-SnO_2-treated MWCNTs.

4. Conclusions

In the present work, we have examined shortening and opening of multi-wall carbon nanotubes produced by catalytic CVD process. Wet milling resulted in a better shortening with open structures than dry milling which easily destroys nanotubes. Using open structures by wet milling, we could fill them with nanoparticles, demonstrating interests in many other applications such as Li-storage.

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