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Abstract. Here we investigate the stabilization process on the active outer/inner surfaces (or the end plane of a graphene sheet) for shortened cup-stacked-type carbon nanotubes caused by annealing, utilizing both analytic and electrochemical techniques. The suggested schematic procedure for loop formation is as follows: (a) formation of single-type loops between neighbouring truncated conical graphene layers at 900–1200 °C through a zipping mechanism after the evolution of hydrogen gas; (b) the transition from single- to multi-type loops above 1500 °C accompanying a decrease in specific surface area.

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Contents

1. Introduction

The end plane of the graphitic layer has been a hot topic in carbon science because of its very special physical, chemical and electronic properties [1]–[3]. The characteristics of these edge sites, especially for the form of tubular-type carbon (carbon nanotubes) [4]–[13], make it possible to utilize them in the fabrication of absorbent materials [14], catalyst–supports [15, 16], field emitters, gas storage components [17] and polymer composites [18, 19]. It is well known that highly reactive edge sites are transformed into stable multi-loops when heat treated at higher temperatures [5, 12, 20, 21].

In this study, we describe the behaviours in the heat treatment induced transition from active edge planes to single/multi-loops for cup-stacked-type carbon nanotubes, as characterized systematically by transmission electron microscopy (TEM), Raman spectroscopy and specific surface area (SSA) and electrochemical techniques.

2. Experimental details

The carbon nanotubes used in this study were produced on a large scale by a catalytic chemical vapour deposition (CVD) method, in particular using the floating reactant method [13]. Comparison to conventional multi-wall carbon nanotubes [22] shows that the main characteristics of these nanotubes are a large hollow core with a wall thickness of about 10–20 nm (figure 1(a)), a round cross-sectional morphology (figure 1(b)) and a tubular morphology formed through the stacking of truncated conical graphene layers (cups), one by one (figure 1(c)), which in turn exhibit a high proportion of open edge sites in the outer/inner surface of the carbon nanotubes.

Carbon nanotubes were shortened through a ball milling process in an effort to utilize the edge sites in the large hollow core. Purification using concentrated hydrochloric acid was carried out three times for 24 h in each case in order to remove the metallic particles incorporated in the tips of the carbon nanotubes. The purified nanotubes were then heat treated between 500 °C and 2800 °C in an argon atmosphere.

High-resolution transmission electron microscopy (HRTEM, JEOL JEM 2010FEF, 200 kV) and Raman spectroscopy (Renishaw Raman image microscope system 1000 equipped with a charge coupled device multi-channel detector and a 514.5 nm argon laser) were used to characterize the formation of single and multi-loops and to examine the structural changes of the cup-stacked carbon nanotubes. Nitrogen adsorption isotherms of the samples were obtained at 77 K using a Micromeritics (ASAP 2010) instrument [23]. From the adsorption isotherms, the surface area and pore (micropore and mesopore) volumes were estimated. Measuring the

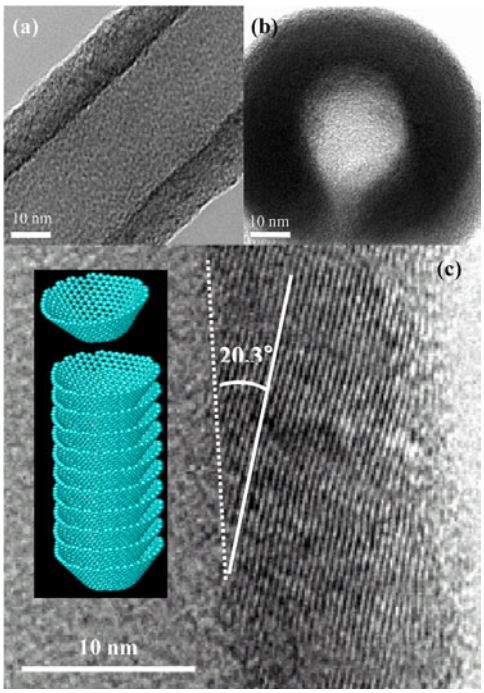

Figure 1. (a), (b) TEM images of pristine carbon nanotubes exhibit a large hollow core and a round cross-sectional morphology, respectively. (c) The HRTEM image shows truncated conical graphene layers with an angle of 20.3° (the inset on the left shows a schematic model for this carbon nanotube).

capacitance in the electrochemical double-layer capacitor (EDLC) was carried out using the method reported earlier (see [24] for the same apparatus and measurement conditions).

3. Results and discussion

For a sample annealed at 2800 °C, two prominent changes are observed:

(1) transformation from a relatively smooth surface to a ragged surface (figure 2(a)) and
(2) the formation of energetically stable loops between adjacent graphene layers from the unstable edge planes in both the outer surface and the inner hollow core (figures 2(b) and (c)).

To ascertain the annealed microstructure of the cup-stacked carbon nanotubes, a simple atomic model based on two truncated cups (figures 3(a) and (b)) was constructed and optimized using silicon graphics. The TEM simulated image (figure 3(c)) shows a clear image of the sidewall and projected vague images of the loops both on the outer surface and on the inner core interface. From these studies, we can conclude that the morphology of the annealed nanotube (2800 °C) is a stacking of truncated onion rings without any internal blockage (with an entirely hollow core).

The main tool utilized in this study in order to understand the transformation from the end planes to stable loops caused by annealing is the measurement of the capacitance in the EDLC because the variation of the capacitance in the EDLC strongly depends on the SSA and on the

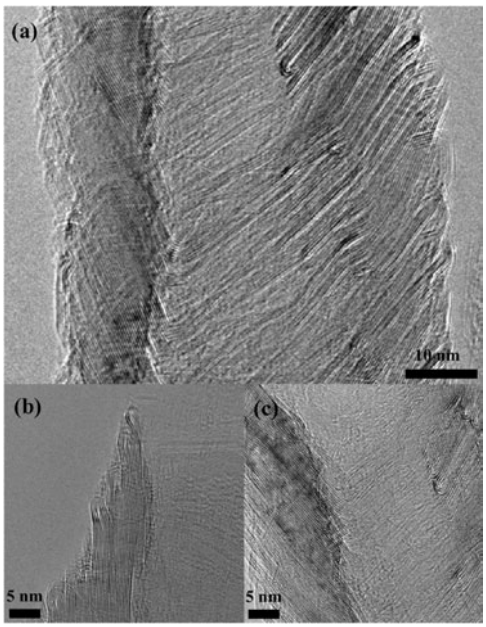

Figure 2. TEM images for carbon nanotubes heat treated at 2800 °C for 1 h: (a) ragged outer/inner surface, (b) multi-loops on the outer surface and (c) multi-loops on the inner surface.

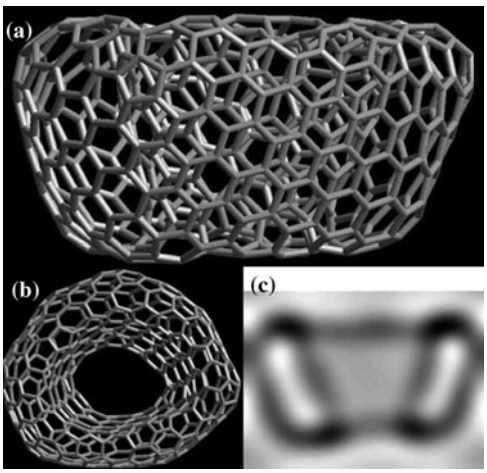

Figure 3. (a), (b) Atomic models of the graphitized onion ring based on two truncated cups at different angles. (c) The TEM simulated image for the atomic model (a JEM2000 (TEM simulation); electron energy = 300 kV, spherical aberration = 2.7 mm, aperture radius = 0.71 $Å^{-1}$, defocus = −80 nm).

pore size distribution of carbon materials [25, 26]. Figure 4 shows the variation of the specific capacitance (F g^{-1}) as a function of annealing temperature (HTT). The capacitor in figure 4 was charged to 3.5 V and discharged at 1 mA cm^{-2} in one case and 40 mA cm^{-2} in a second case. Overall, there is no large difference in capacitance caused by the variation of the discharge current, which indicates a large surface area accessible to the aprotic electrolyte resulting from the

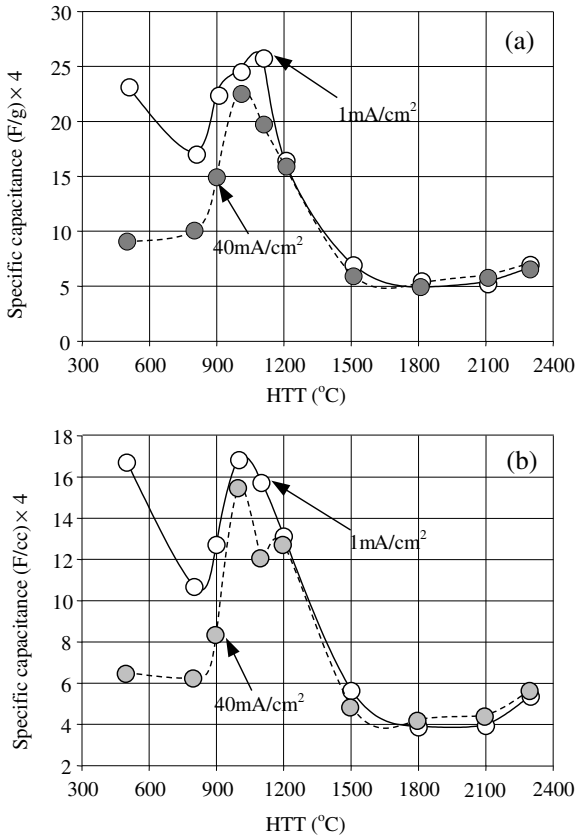

Figure 4. Variation of the specific capacitance with an organic electrolyte (PC) as a function of the heat treatment temperature. (a) Specific capacitance per unit weight (F g^{-1}) and (b) per unit volume (F cm^{-3}). The capacitor is charged to 3.5 V and discharged at 1 mA cm^{-2} in one case and 40 mA cm^{-2} in a second case.

nanosized diameter of the carbon nanotubes (50–150 nm). Remarkable increases were observed in the specific capacitance in the region between 900 °C and 1200 °C, but few changes occurred above 1500 °C. It is concluded that this result is directly connected with the morphological change of the edge sites due to their unique structure. The variation of the SSA (figure 5) confirms the morphological changes of the edge sites on the outer/inner surface of the carbon nanotubes. The abruptly increase in the SSA for the sample at 900 °C is closely related to the development of micropores and might be due to the evolution of hydrogen bonds to the edge planes. Therefore, the edge planes become unstable after evolution of hydrogen gas. As a result, it is believed that the formation of single loops between two adjacent truncated conical layers at around 900–1200 °C and the transformation to multi-loops above 1500 °C are energetically favourable. After the formation of multi-loops, little morphological change is expected, in view of the similar value of the specific capacitance above 1500 °C in figure 4.

The postulation of single and multi-looping at the edge planes is confirmed in figure 6, which shows TEM images of cup-stacked carbon nanotubes heat treated at; (a) 1000 °C, (b) 1200 °C and (c) 1500 °C. No loops are observed for the sample at 1000 °C, but some end planes are relatively undulated, possibly due to the evolution of hydrogen gas. The presence of single or

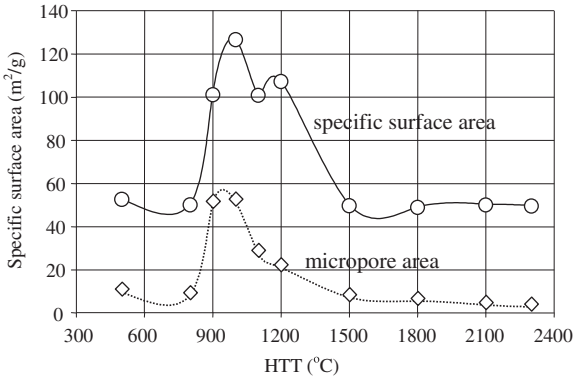

Figure 5. The variation of the SSA and also the micropore area as a function of the heat treatment temperature (established from the nitrogen absorption at 77 K).

multi-loops for the sample at 1200 °C (figure 6(b)) indicates that the energetically unstable end planes are transformed into a stable morphology and, with increasing temperature (figure 6(c)), a large proportion of the end planes begin to show loop structures.

Little change in the Raman spectra was detected above 1500 °C due to the formation of multi-loops (figure 7), which is consistent with the results from the specific capacitance (figure 4). The formation of multi-loops impedes the graphitization of the cup-stacked carbon nanotubes, resulting in a relatively high D peak at 1355 cm^{-1} (the defect mode) and a D′ peak at 1620 cm^{-1} (the shoulder peak) which persist even at 3000 °C, from the first-order Raman spectra. The results in figure 7 also show a peak at 2700 cm^{-1} (2D peak) with a symmetry shape corresponding to incomplete three-dimensional graphitization, indicating less developmental stacking of graphene layers, from the second-order Raman spectra.

The truncated cone angles with respect to the tube axis, measured by means of electron diffraction (ED), lie in the range from 10° to 40° (see figure 1). This is considered to be a factor affecting the Raman spectra because the edge sites of the cup-stacked carbon nanotubes are regarded as edge planes of discontinuous graphite layers with a certain angle. The edge plane spectrum is characterized as having a higher R ($R = I_D/I_G$) value; it has a clearly distinguished D′ peak and a narrower G peak, as compared with those of nanotubes with basal plane edges [27]. The undulated end planes (see the TEM images in figure 6) caused by the evolution of hydrogen gas at 900–1200 °C are clearly related to conspicuous increases of the R and R' values ($R' = I_{D'}/I_G$) (figure 8). For regions above 1500 °C, there is no large change. These results are in accordance with the specific capacitance values.

A model for the relation between single- and multi-loop formations with a growth mechanism staging effect is presented. We postulate that during the growth process, an envelope of truncated conical graphene layers is formed at once from the catalyst surface, consisting of four or more cups. This envelope-type formation occurs due to an interruption in the supply of the critical level of carbon supersaturating the metal catalyst and the difference in rate of carbon supply to the catalyst, which relies on the position of the metal introduced at edge dislocations [28]. In other words, four or more conical graphene layers (about 4–6) are released from the surface of the catalyst when the carbon concentration within it is at a critical level. The resulting cup-stacked carbon nanotubes consist of packets of four or more truncated conical graphene layers which are interconnected forming long tubes. When the tubes are heat treated

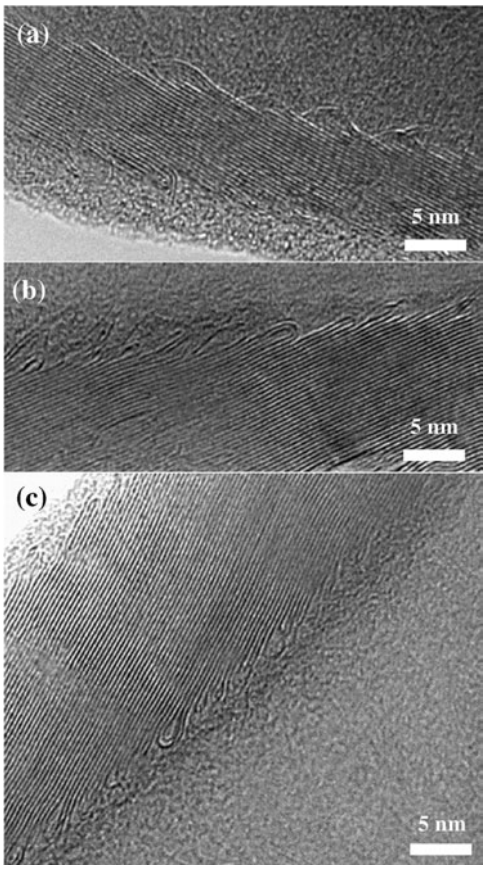

Figure 6. HRTEM images of cup-stacked carbon nanotubes at (a) 1000 °C, (b) 1200 °C and (c) 1500 °C.

at about 900–1200 °C, the single-loop formation only occurs between cups within packets of truncated conical graphene layers and the same occurs at the multi-looping temperature. We believe that the looping occurs due to a slight curvature at the fringes of the cups within the packets. Therefore the distance between the cups is marginally smaller than the distance between the packets and so a preferential looping only occurs within the packets of truncated conical graphene layers. In summary, during the growth process, a staging morphology results in the surface of cup-stacked carbon nanotubes, which restricts the formation of single- and multi-looping structures to occurring only between four or more cups (typically 4–6 cups) only.

4. Conclusions

The process for the morphological variation of cup-stacked carbon nanotubes is suggested mainly from the viewpoint of the formation of single and multi-loops at the edges. The looping structures are clearly seen in TEM (figures 2 and 6). During hydrogen evolution, single loops are formed on the surfaces of the cup-stacked carbon nanotubes at 900–1200 °C. The process of single-loop formation might be carried out through a zipping mechanism [29] because, when chemical bonds are formed at one point, loops are formed easily through the edge planes. With increasing temperature, the single loops become energetically unstable and are transformed into multi-loops

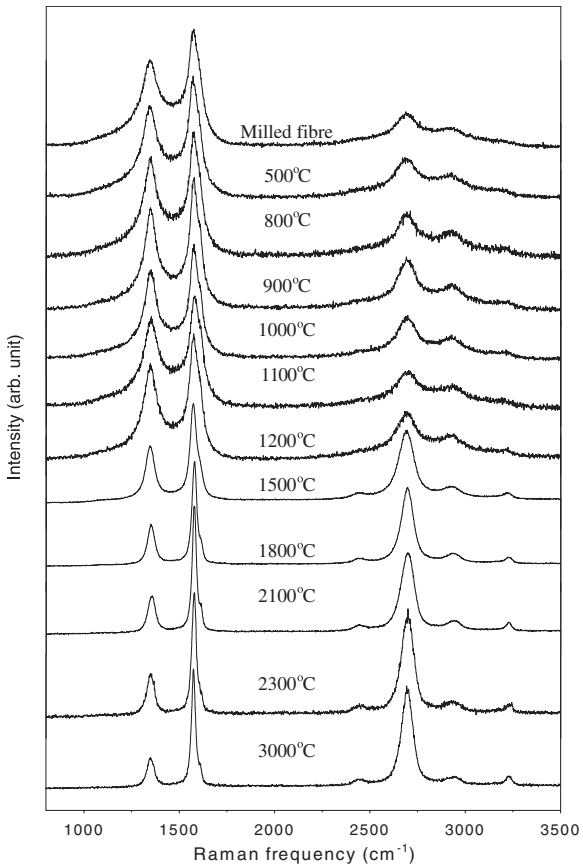

Figure 7. Raman spectra of cup-stacked carbon nanotubes in the range from 500 °C to 3000 °C.

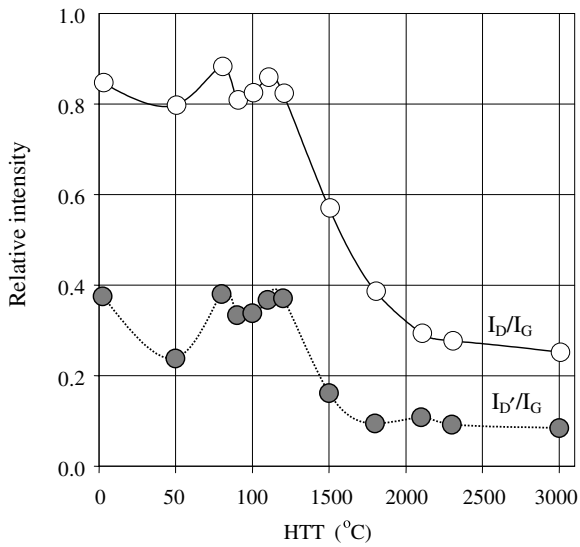

Figure 8. Variations of the relative intensities ($R = I_D/I_G$ and $R' = I_{D'}/I_G$, ratios of the intensity of the G peak to the intensities of the D and D′ peaks, respectively) in the range from 500 °C to 3000 °C.

above 1500 °C like single-wall carbon nanotubes [30]. Carbon nanotubes with an abundance of slit micropores between the surface single loops are obtained by accurate control of the ball milling process and heat treatment. It is expected that the starting temperature for loop formation and also the temperature of transformation to multi-loops will be dependent on the tube diameter, wall thickness, crystallinity, truncated conical angles with respect to the tube axis and the amorphous carbon deposited on the outer surface of the carbon nanotube because these factors determine the thermal stability of the end planes of graphitic layers.

Acknowledgment

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