

## Efficient Cleavage of Carbon Graphene Layers by Oxidants

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The graphene layers at carbon nanotube cap regions are efficiently cleaved by several oxidants (e.g.,  $\text{KMnO}_4$ ,  $\text{OsO}_4$  and  $\text{RuO}_4$ ) in acidic solution at 100 °C, but not by stronger oxidants, such as  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}^+$  and  $\text{H}_2\text{O}_2\text{-H}^+$ .

The basic structure of fullerenes and carbon nanotubes is of carbon graphene layers(s), composed of five- and six-membered rings and C=C double bonds.<sup>1</sup> Up to now, all reported reactions concerning fullerenes and carbon nanotubes occur on the outer surface of the carbon graphene layer by addition to C=C double bond(s).<sup>2</sup> The 'inside' graphene surface chemistry should be as rich as the 'outside' surface chemistry. In addition, the internal hollow space of fullerene cages and carbon nanotubes is expected to act as good host containers. To explore this chemistry, the graphene cage has first to be broken. Cleavage of the fullerene cage has been suggested theoretically,<sup>3</sup> while opening of carbon nanotube graphene layers at the end-cap region was reported by treating nanotubes with  $\text{CO}_2$  or lead as well as with  $\text{O}_2$  at 400–800 °C.<sup>4</sup> The yields are rather low (1–20%), and the mechanisms of these processes are not clear. Herein, we report efficient cleavage (up to 91%) of multiple graphene layers of carbon nanotubes at the end-cap region by various oxidants ( $\text{KMnO}_4$ ,  $\text{OsO}_4$ ,  $\text{RuO}_4$ , etc.) in aqueous solution at 100 °C for 1 h. The mechanism of the cap-opening processes is most probably *via* oxidative cleavage of the C=C double bonds and/or conversion of C=C double bonds to vicinal diols followed by oxidative cleavage of diols. The oxidative cleavage process was also found to be kinetically controlled.

Various oxidants were systematically studied for the ability of cleaving graphene layers of carbon nanotubes (see Table 1). Two powerful oxidants,  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}^+$  and  $\text{H}_2\text{O}_2\text{-H}^+$  were found to be unable to cause opening of carbon nanotube end caps under our experimental conditions.† When  $\text{KMnO}_4$  was used (entry 3, Table 1), ≈ 64%‡ of nanotubes were observed to have open ends. As shown in Fig. 1, a carbon nanotube was converted to a nanostraw with both ends opened. In acidic solution,  $\text{MnO}_4^-$  was reduced to generate  $\text{MnO}_2$  ( $2\text{MnO}_4^- + 2\text{H}^+ \rightarrow \text{MnO}_2(\text{s}) + 3/2 \text{O}_2 + \text{H}_2\text{O}$ ,  $E_0 = +1.41 \text{ V vs. SCE}$ ). Therefore, the cap-opening processes should be considered in terms of both  $\text{MnO}_4^-$  and  $\text{MnO}_2$ . In neutral solution, the amount of  $\text{MnO}_2$

produced *in situ* is strongly reduced due to the very inefficient reduction process of  $\text{MnO}_4^-$ , and only ≈ 15% of carbon nanotubes were observed to have one open end (entry 4, Table 1). When  $\text{MnO}_2$  was added externally to the neutral  $\text{MnO}_4^-$  solution, 59% of carbon nanotubes were observed to have open ends (entry 5, Table 1), indicating the crucial role of  $\text{MnO}_2$  in the nanotube end-cap opening processes. Prolonged heating (1 h) of the neutral  $\text{MnO}_4^-$ - $\text{MnO}_2$ -nanotube suspension solution affords 85% cap opening (entry 6, Table 1). As shown in Fig. 2, several large nanotubes with multiple graphene layers were cleaved open at the end-cap region.

Combinations of  $\text{KMnO}_4$  with  $\text{CrO}_3$  or  $\text{NaIO}_4$  were also able to open the nanotubes end caps, albeit at lower percentages (entries 7, 8, Table 1). Two other powerful oxidants examined were  $\text{OsO}_4$  and  $\text{RuO}_4$ , which are known to be able to oxidatively cleave a single olefin bond in small organic molecules.<sup>5,6</sup> Both oxidants were able to cleave the graphene layers at carbon nanotube end caps with efficiencies compatible to the  $\text{KMnO}_4$  system (entries 9–13, Table 1). As shown in Fig. 3, the large nanotube (treated by  $\text{RuO}_4$ ) has wider open ends than the diameter of the internal hollow space, and both ends are ragged due to oxidative damage. Upon heating for 60 min in  $\text{RuO}_4$  solution, 91% of nanotube end caps are opened; and *ca.* 83% of nanotubes have both ends opened. Although having highest efficiency, the  $\text{RuO}_4$  system is not considered as the best system

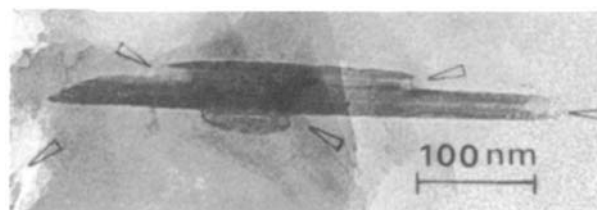


Fig. 1 Transmission electron microscope image of nanotubes treated with  $\text{KMnO}_4$ -10%  $\text{H}_2\text{SO}_4$  solution at 100 °C for 30 min

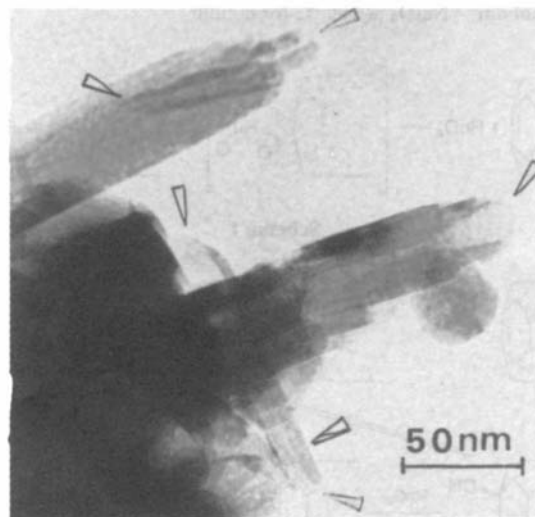


Fig. 2 TEM image of nanotubes, treated with a 0.2 mol  $\text{dm}^{-3}$   $\text{KMnO}_4$  neutral solution in the presence of excess externally added  $\text{MnO}_2$  at 100 °C for 60 min

Table 1 Reagents, conditions, and yields for nanotube cap opening

Reagents	$E_{\text{red}}/V_{\text{SCE}}$	Conditions $T/^\circ\text{C}$ ( $t/\text{min}$ )	% Cap opening <sup>a</sup>
1 $\text{K}_2\text{Cr}_2\text{O}_7^b$	1.04	100 (30)	0
2 $\text{H}_2\text{O}_2$	1.49	100 (30)	0
3 $\text{KMnO}_4^b$	1.20	100 (30)	64 (62:110)
4 $\text{KMnO}_4^b$ (neutral)	0.29	100 (30)	15 (79:14)
5 $\text{KMnO}_4^b$ $\text{MnO}_2^-$	0.29	100 (30)	59 (59:86)
6 $\text{KMnO}_4^b$ $\text{MnO}_2^c$	0.29	100 (60)	85 (16:88)
7 $\text{KMnO}_4^b$ $\text{CrO}_3^b$	0.29	100 (30)	44 (51:41)
8 $\text{KMnO}_4^b$ $\text{NaIO}_4^d$	0.29	100 (30)	< 5
9 $\text{OsCl}_3^e$ $\text{NaIO}_4^d$	0.56	100 (30)	61 (18:28)
10 $\text{OsCl}_3^e$ $\text{NaIO}_4^d$	0.56	100 (60)	81 (8:35)
11 $\text{RuCl}^e$ $\text{NaIO}_4^d$	0.71	100 (30)	66 (8:15)
12 $\text{RuCl}_3^e$ $\text{NaIO}_4^d$	0.71	100 (60)	91 (9:94)
13 $\text{RuCl}_3^e$ $\text{NaIO}_4^d$	0.71	100 (90)	All destroyed

<sup>a</sup> The ratio in parentheses is the number of closed vs. open nanotube end caps observed under TEM. The confidence limit is ±5%. <sup>b</sup> 0.2 mol  $\text{dm}^{-3}$ . <sup>c</sup> In excess the  $\text{MnO}_2$  was generated by heating  $\text{KMnO}_4$  in 20%  $\text{H}_2\text{SO}_4$ , and collected by centrifugation and washed with distilled water prior to use. <sup>d</sup> 70 mg in 0.5 ml solution, partly in solid form which dissolves upon heating. <sup>e</sup> 75 mmol  $\text{dm}^{-3}$ ; upon heating,  $\text{OsO}_4$  ( $\text{RuO}_4$ ) was produced (see refs. 5 and 6, respectively). At the end of the reaction, the solid  $\text{OsO}_2$  ( $\text{RuO}_2$ ) was reduced to soluble  $\text{Os}^{3+}$  ( $\text{Ru}^{3+}$ ) by addition of acidic ascorbate solution.

since the majority of nanotubes were destroyed and much fewer nanotubes were observed under TEM. Further heating for 90 min results in complete destruction of the nanotubes.

These open-ended carbon nanotubes processed by the above oxidants share one significant common feature, that is, a larger internal diameter near the open end than within the tube (see Figs. 1–3). This indicates two important aspects: the entrance of the oxidant aqueous solution into the internal hollow space of open ended nanotubes,<sup>§</sup> and a higher tendency of oxidation of the internal graphene layers (walls) than the outer layers. The former observation confirms theoretical predictions that polar molecules near the open end can induce polarization along the long axis of nanotubes, and move into the internal hollow space.<sup>7</sup> The latter observation can be rationalized by the previous conclusion derived from both theoretical calculations<sup>8</sup> and the experimental observation<sup>1,9</sup> that local strain is one of the major driving forces for chemical reactions. The inner-most layers of a nanotube have larger curvature (higher strain) than the outer layers, and therefore are more readily oxidatively cleaved.

The structure of carbon graphene layers is composed of adjoining C=C double bonds. Therefore, the cleavage mechanism by the above oxidants is believed to follow similar patterns as in small olefin molecules (*vide infra*). In the case of RuO<sub>4</sub>, the C=C double bonds on graphene layers first form a ruthenium ester<sup>6</sup> adduct followed by C–C bond cleavage to form two ketone functional groups (Scheme 1).

For KMnO<sub>4</sub><sup>10</sup> and OsO<sub>4</sub>,<sup>5</sup> the C=C double bonds at the nanotube end caps are first converted to vicinal diols *via* formation of the manganese<sup>10</sup> (or osmium<sup>5</sup>) esters, followed by oxidative cleavage of the vicinal diols by MnO<sub>2</sub>,<sup>11</sup> CrO<sub>3</sub><sup>12</sup> or IO<sub>4</sub><sup>–13</sup> (Scheme 2).

This study clearly shows that RuO<sub>4</sub>, OsO<sub>4</sub> and MnO<sub>4</sub><sup>–</sup>–MnO<sub>2</sub> systems are able to consecutively cleave several

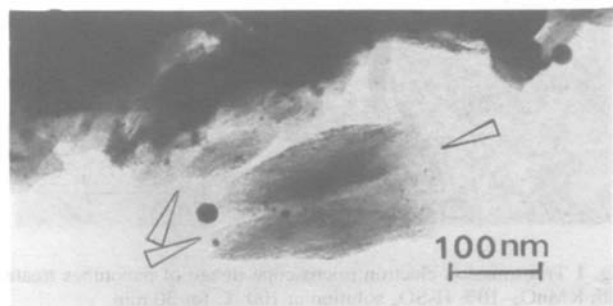
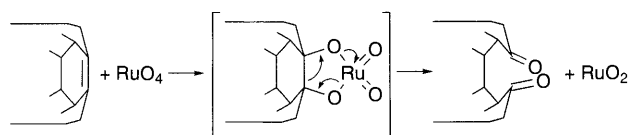
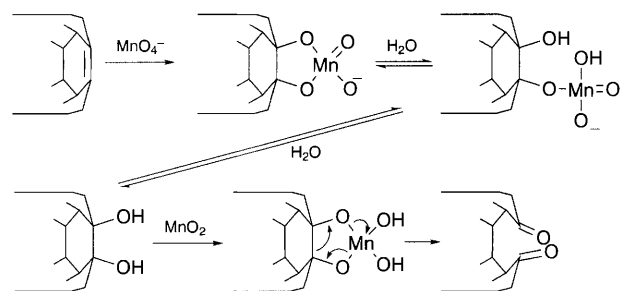


Fig. 3 TEM image of nanotubes treated with 75 mmol dm<sup>–3</sup> RuCl<sub>3</sub>–0.65 mol dm<sup>–3</sup> NaIO<sub>4</sub> at 100 °C for 60 min



Scheme 1



Scheme 2

adjoining olefin bonds and graphene layers with high efficiencies.

While K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>–H<sup>+</sup> and H<sub>2</sub>O<sub>2</sub>–H<sup>+</sup> are stronger oxidants they are unable to cleave graphene layers indicating that the oxidative cleavage process is not thermodynamically, but kinetically controlled.

In summary, several oxidants (KMnO<sub>4</sub>, OsO<sub>4</sub>, RuO<sub>4</sub>, etc.) were shown to be able to consecutively cleave adjoining olefin bonds and graphene layers on the carbon nanotube cap regions. The oxidation process is believed to occur *via* conversion of C=C bonds to diols followed by oxidative cleavage, and is kinetically controlled. The results presented above clearly indicate the feasibility of opening windows(s) on fullerene cages,<sup>3</sup> and the methods applied here provide a new avenue for the study of ‘inside cage’ fullerene chemistry. Currently we are actively pursuing this possibility.

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## Footnotes

† In a typical experiment, *ca.* 1 mg of nanotubes (MER Corporation, length 0.1–100 μm, diameter 3–50 nm) was put in 0.5 ml of 0.2 mol dm<sup>–3</sup> oxidant–10% H<sub>2</sub>SO<sub>4</sub> aqueous solution, and ultrasonicated for 5 s, followed by heating in an oil-bath at 100 °C for 30–60 min. The solution was then cooled to room temp., and the carbon nanotubes were collected by centrifugation, washed with distilled water and methanol. A drop of nanotube–methanol suspension solution was then placed on to a carbon thin film coated copper grid for transmission electron microscope (TEM) measurements. The TEM images were obtained from a Hitachi (model: H-600-3) operated at 75 kV.

‡ Quoted percentages are the ratio of the numbers of closed vs. open nanotube end caps observed under TEM.

§ This is in sharp contrast to a previous report<sup>4</sup> that molten lead atoms are unable to enter the hollow internal space of carbon nanotubes.

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