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LETTER

# Oxidation resistance of multi-walled carbon nanotubes purified with sulfuric and nitric acids

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Discovered by Iijima in 1991 [1], carbon nanotubes (CNTs) have been attracting increasing research interests due to their exceptional physical, chemical and mechanical properties. CNTs have shown application potentials in the field of composite reinforcements, display panels, nanodevices and hydrogen storage [2]. A number of research efforts [3–9] have focused on the purification of CNTs because as-prepared CNTs often contain impurities, such as amorphous carbon, catalyst metals, and fullerene or graphite particles. Among the abundant purification methods, refluxing in concentrated $H_2SO_4/HNO_3$ (3:1) have been considered facile for the selective removal of impurities from CNTs with little destruction of tube walls [3, 4].

In some cases, high temperature gasification is needed after CNTs are refluxed in $H_2SO_4$ and/or $HNO_3$. Delpeux et al. [5] treated single walled carbon nanotubes (SWCNTs) under $CO_2$ at 525 °C in order to remove the debris of disordered carbon after SWCNTs were refluxed in $HNO_3$. Valentini et al. [6] purified SWCNTs by a treatment with concentrated $HNO_3$ acid, and then oxidized in air. In these cases, a high oxidation resistance of CNTs in oxidative gases is important, since this can ensure the selective removal of disordered carbon from acid purified CNTs. Accordingly, it is necessary to know the effect of acid treatment on the oxidation resistance of nanotubes. A few works has been done to build the relationship between acid treatment and oxidation characters of CNTs. Zhang et al. [7] reported that oxidation temperature of SWCNTs in oxygen increased due to the removal of catalyst metal by refluxing in concentrated $HNO_3$ acid for 1 h. If the refluxing time duration was 4 h, the oxidation temperature decreased because surface groups on nanotube walls are more reactive toward oxygen. However, Huang et al. [8] pointed out that concentrated $HNO_3$ and/or HCl purified multi-walled carbon nanotubes (MWCNTs) were more easily oxidized in air than the raw ones. So further research works are needed to evaluate the effect of purification on the oxidation process of CNTs. In this letter, MWCNTs are purified using concentrated $H_2SO_4/HNO_3$ acids, and then their oxidation characters were investigated. The results revealed that oxidation resistance of MWCNTs was improved after they are purified.

MWCNTs with an average diameter of 28 nm were provided by Shenzhen Nanoport Corparations (China). As-supplied MWCNTs were measured by Axios-PW4400 X-ray fluorescence spectrometers (XRF) to determine their compositions. As-supplied MWCNTs were purified by $H_2SO_4/HNO_3$. Detailed purification process can be seen elsewhere [9]. In brief, MWCNTs were refluxed in concentrated $H_2SO_4/HNO_3$ (3:1) using a magnetic stirrer for 48 h. Then extra acid was removed by filtration through a porous membrane and the deposits were washed with distilled water until the pH value reached 7. Finally, the deposits were dried in a vacuum furnace at 150 °C overnight. Microstructure of MWCNTs was observed in a Tecnai 20 TEM equipped with an energy dispersive spectrometry (EDS). Oxidation process of the dried MWCNTs was carried out in air using a Netzsch STA 449c DSC/TG. The flowing rate of air was 50 mL/min and the heating rates were 5, 20 and 40 °C, respectively.

XRF measurement shows that as-supplied MWCNTs contain the following elements (mole fraction): C 98.68%, Ni 0.33%, La 0.03%, O 0.90%, Co 0.02%, Fe 0.02%,

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S 0.02%. Figure 1 is the TEM micrograph of the MWCNTs. It can be seen that the surfaces of the as-supplied (Fig. 1a) and purified (Fig. 1b) MWCNTs are smooth, revealing that the purification treatment does not destruct CNT walls. Only the impurity agglomerates shown in Fig. 1a have been selectively removed by $H_2SO_4/HNO_3$ purification. EDS traces (Fig. 1c) show that impurity agglomerates in Fig. 1a contain Ni and C (Cu and Zn peak appear since the copper grid is used to hold the MWCNTs). As the morphology of carbon in the agglomerates is different from that of CNT, it can be deduced that the impurity agglomerates contain amorphous carbon together with Ni.

Figure 2 shows the thermogravemitric (TGA) and derivative thermogravemitric (DTG) traces of as-supplied and purified MWCNTs. There is only one peak in the DTG traces. The peak temperature of MWCNTs increases with the increasing of heating rate. At a heating rate of 5 °C/min, the oxidation peak temperatures of the as-supplied and purified MWCNTs are 603.87 and 629.62 °C, respectively. This shows that the oxidation resistance of MWCNTs is enhanced after they are purified using $H_2SO_4/HNO_3$ acids. At heating rates of 20 and 40 °C/min, however, the peak temperatures of the as-supplied and purified MWCNTs exhibit comparatively little difference. This means they show similar oxidation resistance at high heating rates.

It is reported that gasification process of MWCNTs with air is a first order reaction [10] and the reaction obeys an Arehenius-type relation [11]. So oxidation reaction rate of MWCNTs with air can be described as:

$$\frac{dx}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} (1 - x) \tag{1}$$

where $x$, $T$, $A$, $\beta$, $E$ and $R$ are the weight, temperature, frequency factor, heating rate, activation energy and gas constant, respectively. The Napierian logarithm of Eq. 1 is:

$$\ln \beta = -\frac{E}{RT} + \left[ \ln A + \ln(1 - x) - \ln \frac{dx}{dT} \right] \tag{2}$$

Acording to the TG/DTG traces in Fig. 2, the weights ($x$) corresponding to oxidation peak temperatures ($Tp$) differ very little at different heating rates. So Eq. 2 defines a linear relation between $\ln\beta$ and $Tp^{-1}$, as is shown in Fig. 3. Accordingly, the $E$ and $A$ of the reaction can be determined by the slope and intercept of the lines. In Fig. 3, it can be seen that $\ln\beta$ and $Tp^{-1}$ obeys a fairly well linear relation, proving that Eq. 2 is reasonable to depict the reaction process of MWCNTs with air.

The activation energy and frequency factor of the as-supplied and pufied MWCNTs are listed in Table 1. It can be seen that activation energy and frequency factor of MWCNTs increase after purification treatment, implying that purified MWCNTs are less sensitive to oxidation. Calculated by $k = A \times \exp\{-E/(RT)\}$, the reaction constant of the as-supplied and purified MWCNTs are plotted in Fig. 4. It clearly shows that the reaction constant of purified MWCNTs is much higher than that of the as-supplied ones. In addition, the reaction constants of both MWCNTs are small below 800 °C, then increase rapidly with

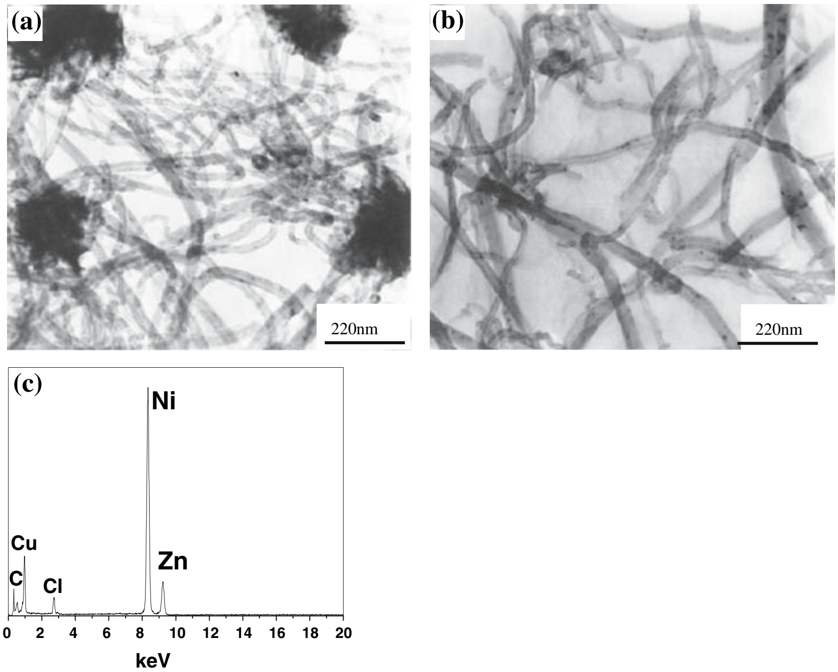

**Fig. 1** TEM micrograph of the as-supplied and purified MWCNTs: (**a**) as-supplied; (**b**) purified; (**c**) EDS of impurity agglomerate

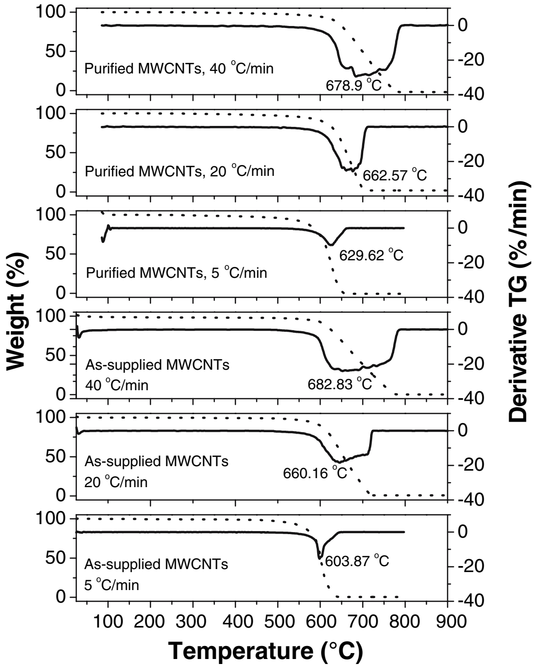

**Fig. 2** TGA and DTG traces of the as-supplied and purified MWCNTs

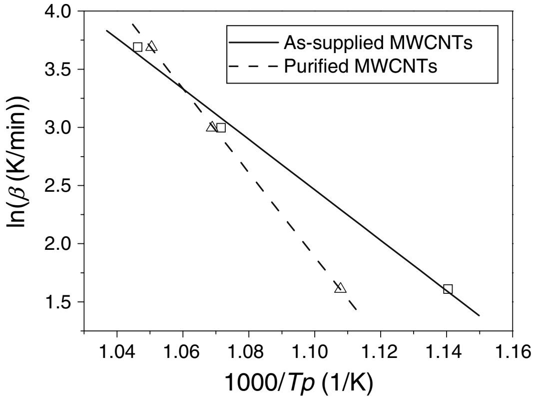

**Fig. 3** Ln$\beta$ vs. 1000/*Tp* of the as-supplied and purified MWCNTs

**Table 1** Oxidation kinetic parameters of as-supplied and purified MWCNTs

| | As-supplied | Purified |
|---|---|---|
| Activation energy (kJ/mol) | 166.38 | 287.13 |
| Frequency factor ($S^{-1}$) | $1.445 \times 10^7$ | $1.259 \times 10^{14}$ |

increasing temperature. The higher reaction constant of the purified MWCNTs implies that their oxidation process may proceed at a higher rate. This is consistant to the fact that there is little difference between the oxidation peak temperature of as-supplied and purified MWCNTs at high heating rate, as has been shown in Fig. 2.

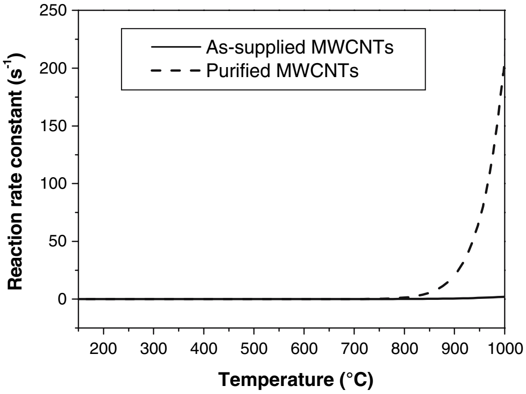

**Fig. 4** Reaction constant of as-supplied and purified MWCNTs

Many factors play a part in the oxidation resistance of CNTs, including the graphitization degree [8], content of catalyst metal [7] or surface groups [3, 4, 8], and the local heat effects [7, 12]. In our experiment, purification treatment does not seem to affect the graphitization degree of nanotubes. As the content of catalyst metal in the as-supplied MWCNTs is so low that purification has few effects on the oxidation of nanotubes. Much research works prove that concentrated $H_2SO_4/HNO_3$ treatment can result in high content of oxygen containing surface groups on MWCNT walls [3, 4]. As the surface groups are more susceptible to oxidation than nanotubes [7], purified MWCNTs should be more easily oxidized than as-supplied ones. However, purified MWCNTs are less sensitive to oxidation, as shown in Fig. 2. So the local heat effects must be the main factor dominating the oxidation process of MWCNTs. Figure 1a shows that as-supplied MWCNTs contain many agglomerates that is made of amorphous carbon and Ni. When the as-supplied MWCNTs are heated in air, the pre-ignition of the amorphous carbon release heat and cause the local temperature to rise. This will arouse the early combustion of nanotubes. As a result, as-supplied MWCNTs are less resistant to air oxidation than purified ones.

In conclusion, concentrated $H_2SO_4/HNO_3$ acids are effective to removes the amorphous carbon and catalyst metals in MWCNTs. The local heat released by pre-ignition of amorphous carbon is a key factor that affects the oxidation process of MWCNTs. Purified MWCNTs exhibit higher activation energy and rate constant and show improved oxidation resistance in air than the as-supplied ones. This makes it possible for $H_2SO_4/HNO_3$ acids to be used as a first step purification agent, giving rise to an improved oxidation resistance of MWCNTs.

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