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Effective control of nanodefects in multiwalled carbon nanotubes by acid treatment

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ABSTRACT

The defect-type evolution and gradual increase in nanodefects in the outer walls of multiwalled carbon nanotubes (MWCNTs) in a chemically oxidizing environment were thoroughly investigated using a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). A fairly low temperature of 323 K was employed for the acid treatment, and this limited the reaction rate to provide a mild acidic environment for gradual chemical oxidation compared to commonly used treatment conditions. High-resolution transmission electron microscopy (HRTEM) observations clearly demonstrated the formation of groove-type defects in the outer walls of MWCNTs in the early period around 0.5–3 h, followed by a morphological change into circumference-type defects and further into unzipped graphene nanoribbons. A unique parabolic variation in the intensity ratio of D and G bands (I_D/I_G) was observed. This observation supports the gradual oxidation of graphitic walls with increasing acid treatment time and corresponds well with the formation and evolution of nanodefects. Herein, the appropriate acid treatment time that would result in an effective number of nanodefects via suitable carboxyl functionalization, providing preferential nanocarbide sites for interfacial improvement as well as uniform dispersibility of MWCNTs, has been discussed.

1. Introduction

Carbon nanotubes (CNTs), first discovered in 1991 [1], possess excellent properties such as high strength, high elastic modulus, and superior thermal and electrical conductivity [2,3]. Research on CNTs-reinforced metal matrix composites has attracted extensive attention because of the dramatically improved properties of the matrix [4–6]. For instance, CNT–Al composites with high mechanical strength and low weight are extraordinarily promising candidates for applications in electronic devices, and automotive and aerospace industries [7].

However, the difficulty in achieving a uniform dispersion of CNTs and the poor bonding at the CNT–host metal interface severely hinder the development of CNT–metal matrix composites because the excellent properties of CNTs cannot be fully exploited. An effective approach to improve this interfacial bonding is the formation of chemical bonding at the interface. Thus, the presence of carbide nanostructures could improve the interfacial bonding in CNT–metal matrix composites [5,8–11]. Such nanostructures might be formed at active sites such as structural disorders, amorphous carbon layers, and tips of CNTs during composite fabrication or subsequent annealing [8–11]. To the best of our knowledge, the formation of carbide nanostructures on CNTs is still a topic of controversy. Very recently, Hwang et al. found carbide nanocrystals at structural disorders in CNT–nickel composites synthesized by molecular level mixing [12]. However,

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the interfacial reaction between the metal matrix and CNTs has not been fully understood yet. In addition, the quantitative evaluation of load transfer at the CNT–metal matrix interface with or without nanocarbides has not been carried out yet. Therefore, the effect of nanocarbides on the strength of CNT–metal matrix composites is still not clear. This lack of clarity is attributed to several factors, including lack of precise observations of the type and size of nanodefects in CNTs produced during acid treatment; lack of clear high-resolution transmission electron microscopy (HRTEM) photographs showing evidence for the existence of nanocarbides at the CNT–metal matrix interface; and lack of HRTEM observations of nanocarbide properties, i.e., dimension, category, and quantity, resulting in lack of comprehension on the nanocarbide formation mechanism. It is quite important that these factors are prevented in order to exploit the intrinsic strength of CNTs. For the interfacial phenomena in CNT–metal matrix composites to occur satisfactorily, it is imperative to produce and control nanodefects sited on the outer walls of CNTs, where dangling bonds of carbon atoms are preferentially reactable with metal atoms.

It is well known that acid treatment is an effective and common method for modifying the surface of CNTs, not only to purify them but also to improve their dispersion by generating functional groups in their outer walls. Unfortunately, concentrated attention regarding chemically oxidized CNTs has usually been focused on removing impurities within CNTs [13–15], improving dispersion of CNTs in a medium [16–18], and unzipping CNTs into graphene nanoribbons [19–21]. Relatively fewer researches have been reported on the relationship between the formation of nanodefects (type, quantity, size, etc.) and acid-treatment conditions (time or temperature). Moreover, a few challenges have to be overcome for positively utilizing nanodefects in the outer walls of CNTs, for example, to form alterative nanocarbides for improving interfacial bonding in CNT-metal matrix resulting in the improvement of load-bearing capacity of the CNTs.

Recently, we succeeded in fabricating novel multiwalled carbon nanotube (MWCNT)-Al composites characterized by a highly strain/dislocation-free microstructure, in which acid-treated, individually dispersed MWCNTs having a clean/intimate interface with the matrix were mostly aligned along the extrusion direction [22]. These hybrid composites represent an unique clean system, using which we can eventually demonstrate the contribution of load transfer to MWCNTs on the tensile response of Al in the effective absence of processing-induced work hardening, defects, and interfacial impurities [22]. If we can intentionally introduce a controlled number of nanodefects in the outer walls of CNTs, and can form appropriate carbide nanostructures at the nanodefect sites by precisely controlled heat treatment, more enhanced load transfer can be obtained from the CNTs to the matrix.

The rate of chemical oxidation of CNTs is closely related to the treatment temperature, and commonly, temperatures rather higher than 373 K are used for their acid treatment [13,14,23–29]. This is because the purification and functionalization of CNTs are the primary objectives. However, higher treatment temperatures easily cause significant weight loss in initial CNTs by converting sp^2-hybridized carbon atoms to oxidized sp^3 ones, as well as result in the formation of a large amount of amorphous carbon [24,30]. In addition, the imperfect outer layers of CNTs resulting from chemical vapor deposition (CVD) growth can be rapidly attacked by oxygen atoms in a hyperthermal acid mixture, leading to serious degradation of sidewalls even for a short treatment time (<1 h) [18]. For this reason, not enough research has been conducted for clearly identifying the type and size of nanodefects induced during acid treatment, particularly during the early oxidation stage.

In this study, we employed a relatively lower temperature of 323 K, compared with commonly used treatment conditions [13,14,23–30], for treating MWCNTs using a mixture of sulfuric acid (H_2SO_4) and nitric acid (HNO_3). This lower temperature played a critical role in reducing the reaction rate and provided a mild acidic environment for the gradual chemical oxidation and creation of nanodefects in the outer walls of MWCNTs. The degree of MWCNT damage was carefully monitored and the morphology evolution of nanodefects was observed by HRTEM. On the basis of an analysis of the type and quantity of nanodefects by controlling the treatment time, a mechanism for the correspondence between nanodefects and oxidation conditions has been discussed in detail. The appropriate acid treatment time that would result in an effective number of nanodefects via suitable carboxyl functionalization, providing preferential nanocarbide sites for interfacial improvement as well as uniform dispersibility of MWCNTs, is also discussed.

2. Experimental

2.1. Raw materials

The pristine MWCNTs were provided by Hodogaya Chemical Co. Ltd., Japan by means of the catalytically chemical vapor deposition, and subsequently treated by thermal annealing at more than 2200 °C [31]. The average diameter of the pristine MWCNTs is about 70 nm calculated by HRTEM photographs, and the average length is around 7.7 μm measured by FESEM photographs. The sulfuric acid (H_2SO_4, 97%) and nitric acid (HNO_3, 61%) were obtained from Wako Industries, Japan.

2.2. Purification and acid treatment of MWCNTs

In order to remove impurities like amorphous carbon and metal catalyst without damages, pristine MWCNTs were initially purified by concentrated HNO_3. 5 g pristine MWCNTs were suspended in 300 mL HNO_3 and ultrasonicated in water bath equipped with a mechanical stirrer at 323 K for 12 h. Then the slurry was scoured with deionized water until pH to neutral and collected on the filter paper. The purified MWCNTs were completely dried under air at 373 K for 12 h. After that, acid treatment was employed to form nanodefects in outer walls of MWCNTs. 2 g purified MWCNTs were dissolved by 240 mL acid mixture (HNO_3:H_2SO_4 = 1:3, v/v) in ultrasonic bath equipped with the mechanical stirrer at 323 K from 0.017 h to 9 h, followed by washing, filtrating and drying as the same conditions in purification.