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Controlling the number of walls in multi walled carbon nanotubes/alumina hybrid compound via ball milling of precipitate catalyst

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ABSTRACT

This paper reports the influence of milling time on the structure and properties of the precipitate catalyst of multi walled carbon nanotubes (MWCNT)/alumina hybrid compound, produced through the chemical vapour deposition (CVD) process. For this purpose, light green precipitate consisted of aluminium, nickel(II) nitrate hexahydrate and sodium hydroxide mixture was placed in a planetary mill equipped with alumina vials using alumina balls at 300 rpm rotation speed for various milling time (5–15 h) prior to calcinations and CVD process. The compound was characterized using various techniques. Based on high-resolution transmission electron microscopy analysis, increasing the milling time up to 15 h decreased the diameter of MWCNT from 32.3 to 13.1 nm. It was noticed that the milling time had a significant effect on MWCNT wall thickness, whereby increasing the milling time from 0 to 15 h reduced the number of walls from 29 to 12. It was also interesting to note that the carbon content increased from 23.29 wt.% to 36.37 wt.% with increasing milling time.

1. Introduction

Carbon nanotubes (CNT) have extraordinary and multifunctional properties due to their unique physical properties, and were first recognized by Sumio Iijima [1]. In the Polymer Matrix Composite (PMC) production industry, for example, CNT has been utilized as fillers. Similarly, several works [2–9] have successfully used CNT as fillers and binders to improve the mechanical, thermal and electrical properties of polymer matrix composites. The main drawback in the employment of CNT as fillers is the high cost involved in the production process, and its low yield per synthesis. Less costly methods to produce CNT have been investigated [10–13], and eventually, the chemical vapour deposition (CVD) process [14] was found to be the most efficient way of producing CNT in large quantity. In CVD process, the chemical reactions of a gaseous precursor were reacted on a heated substrate surface to produce the desired deposit. The fabrication of CNT depends on temperature, pressure, feedstock gas, reaction time, gas flow rate and the catalyst used during the process. Recently, hybrid CNT filler via CVD has become an acceptable approach towards maximizing the effect of reinforcement. Several works [15–18] have been published regarding this approach. In these initial studies [15,16], it has been demonstrated that hybrid CNT filler is capable of imparting significant reinforcement effect, but is yet to be optimized in terms of the catalyst size and shape. In different studies on CNT produced through CVD [19,20], it was shown that the size of CNT was influenced by the growth temperature and carbon reactant supplies which depend on the catalyst volume to surface area ratio has been reported.

Despite the fact that the CVD method for producing CNT has been of interest to the scientific field, the effect of the particle size on the precipitate catalyst mixture prior to CVD has not often been reported. We believed that CNT formation via CVD is influenced by the particle size of the precipitate catalyst mixture before the CVD process. Theoretically, CNT size is reduced with catalyst size reduction for all CNT growth in the CVD system [21–23]. As the construction of a nanostructure is the main objective of this study, information on geometry size and shape of carbon

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nanotubes is essential. Milling is considered as a promising technique to reduce particles size with regard to the size of precipitate catalyst. Consequently, Esawi and Morsi [24] conducted a study on the effectiveness of dispersing nanotubes within aluminium (Al) matrix at various milling times. The relationship between the dispersion level of carbon nanotubes and milling time was studied [25], and it was discovered that the strength of the mechanical properties in Al-CNT composites is enhanced by the dispersion of nanofibers and aluminium precipitation. It has also been reported that milling variables affect the dispersion, dimension and interface structure of Al-multi walled carbon nanotubes (MWCNT) composites [26,27]. Milling variable with insufficient milling intensity hampers consolidation, while milling with intermediate intensity results in a strong and firm interface and milling with excessive intensity embeds the nanotubes without infiltration [26,27]. In a separate study [28], it was reported that milling of MWCNT broke up large aggregates into a number of small aggregates as well as exfoliate individual nanotubes to ease dispersion. The milling process typically involves effective use of variables to achieve the desired form of a nano-sized microstructure. The diversity of milling indicates their capacity and operation speed, as well as their ability to vary temperatures and minimize contamination of the ball-to-powders [29]. The most favourable conditions that can be achieved by varying the milling time depend on the type of mill, size of the grinding medium, temperature during milling and ball-to-powder ratio [29]. The correlation between milling time, particle size and CNT yield was investigated and discussed.

Carbon nanotubes are commonly categorized as single-walled (SWCNT), double-walled (DWCNT) and MWCNT. SWCNT, DWCNT and MWCNT correspond to the graphite layers rolled up in the CNT. Based on its graphite layers, the electronic properties of CNT vary significantly depending on the chirality and the number of graphene walls. SWCNT can either be semiconducting or metallic due to the chirality of the single wall and its typical diameter, with just few nanometers. Meanwhile, MWCNT is always metallic. Therefore, SWCNT is mostly used for electronic applications due to its electronic properties, which vary with their chirality, while MWCNT is usually used in composites to enhance the mechanical and thermodynamic properties. However, the production of MWCNT is much cheaper than SWCNT. Based on the beneficial use of MWCNT, a new research study should be performed. Moreover, it requires creating a new MWCNT with great electronic properties through controlling the number of wall in CNT.

In this study, we attempted to control the geometry of CNT by controlling the particle size of the catalyst mixture through the ball milling technique. Then, the synthesis of multi-walled carbon nanotubes/alumina hybrid compound was achieved via CVD process. The morphological and structural changes in MWCNT/alumina (Al_2O_3) hybrid compound due to various milling times were investigated in detail. Our aims in the present study were to control the morphology of the grown CNT (size, number of wall) and to establish the correlation between catalyst size, CNT and morphology. In order to achieve these goals, we used the field emission scanning electron microscope (FESEM), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra and thermal conductivity to characterize the hybrid compound.

2. Experimental

In the preparation of the catalyst, distilled water was used to mix the aluminium powder [0.38 mol, 99% purity] and nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) [0.01 mol, 98% purity], while sodium hydroxide (NaOH) [0.01 mol, 98% purity] was dissolved in 50 ml distilled water with constant stirring. The formed green precipitate was aged at room temperature for 24 h without stirring before the colloid ($Ni(OH)_2 + Al(OH)_4$) was attained. It was washed, filtered and dried for 2 h at 80 °C. The reactions involved were as follows:

$$Al \xrightarrow[NaOH]{} Al(OH)_4 \quad (1)$$

$$Al(OH)_4 \xrightarrow[-H_2O]{} Al_2O_3 \quad (2)$$

The elemental nickel (II) oxide (NiO) was formed according to chemical reactions 3 and 4.

$$Ni(NO_3)_2 \cdot 6(H_2O) \xrightarrow[NaOH]{} Ni(OH)_2 \quad (3)$$

$$Ni(OH)_2 \xrightarrow[-H_2O]{} NiO \quad (4)$$

The light green precipitate was then milled in a planetary ball-mill for 5, 10 and 15 h at room temperature. The details of the milling parameters are given in Table 1. 300 rotation speed of vial (rpm) was selected due to the range (65–80%) of the critical speed (CS), which was calculated as follows:

$$CS = \frac{42.3}{\sqrt{D_{mill}}} \quad (5)$$

where D_{mill} represents the mill diameter (mm). Furthermore, the minimum diameter, $D_{ball\ min}$ (mm) of ball size was calculated using the equation:

$$D_{ball\ min.} = 10 D_{ball\ max.} \sqrt[2]{\frac{\sigma^2}{0.128 E \rho_{ball} D_{inner}}} \quad (6)$$

where $D_{ball\ max.}$ represents the maximum size of feed (mm), σ is the compression strength (MPa), E is the modulus elasticity (MPa), ρ_{ball} is the density of ball material (kg/m^3) and D_{inner} is the inner diameter of the vial mill (mm). In most cases, the ball diameter size ranges from $D_{inner}/18$ to $D_{inner}/24$. Meanwhile, the ball to powder ratio (BPR) was calculated as follows:

$$BPR = \frac{M_{ball}}{M_{powder}} \quad (7)$$

where M_{ball} represents the mass of the ball (g) and M_{powder} is the mass of the powder in the vial (g).

Then, the catalyst was calcined at 900 °C, which is the most appropriate temperature for NiO-Al_2O_3 interaction in order to achieve further reaction during methane decomposition, as reported elsewhere [11].

$$NiO \xrightarrow[H_2]{} Ni \quad (8)$$

To synthesize CNT through CVD process, the NiO-Al_2O_3 needed to be annealed at 400 °C for 2 h in H_2 gas. It was done to initiate the growth of nanotubes. Although both NiO and Al_2O_3 were annealed in H_2 gas, only NiO reacted with H_2, which led to small amount of crystalline Ni before CNT growth, indicating that the following mechanism (chemical reaction 8) represented the pathway for Ni in the sample. Hou and others [30] pointed out in their detailed study that Al_2O_3 as highly resistant to oxidation and coatings designed

Table 1
Details of milling parameters.

Ball mill machine conditions	Unit	Planetary mill Retsch (PM100)
Rotation speed of vial	rpm	300
Time	hour	5, 10, 15
Vial material	–	Alumina
Ball material	–	Alumina
Diameter of balls	mm	10
Number of balls	–	35
Balls to powder ratio (BPR)	–	1:1