



Facile and effective aluminium nitride anti-oxidation coating for carbon nanotubes



Yue Han^{a,b}, Heng Zhou^a, Shan Li^{a,b}, Li Ye^{a,*}, Fenghua Chen^a, Yuanhao Li^a, Tong Zhao^{a,*}

^a Laboratory of Advanced Polymeric Materials, Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, PR China

^b University of Chinese Academy of Sciences, 100049 Beijing, PR China

ARTICLE INFO

Article history:

Received 1 April 2015

Revised 6 June 2015

Accepted in revised form 12 June 2015

Available online 14 June 2015

Keywords:

Carbon nanotubes

Aluminium nitride

Nanostructure

Oxidation resistance

ABSTRACT

Carbon nanotubes (CNTs) were coated by aluminium nitride (AlN) via a simple gradual sedimentation and ceramization route. Following a designed sequence, CNTs were coated with aluminium-containing precursor and carbon source, which were dissolved in a mixed solution of isopropanol and toluene; the subsequent pyrolysis and carbothermal nitridation generated AlN layer onto the CNT surface. The coating thickness was tunable from 1 to 2 nm, while maintaining defect free. Thermogravimetric analysis revealed that the onset oxidizing temperature of the product delayed from 525 to 707 °C, and more than 90% CNTs survived the oxidation. Furthermore, the coating mechanism was proposed and verified.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) are known as possessing excellent mechanical, electrical and thermal properties [1–3]. However, severe oxidation will occur when they are heated to 500–550 °C, which hinders their application in high temperature environments. The coupling of CNTs and ceramic proves an effective way for protecting CNTs from oxidation, and kinds of ceramics have been successfully coated onto CNTs [4–16]. The onset oxidation temperature (T_{onset}), along with the improvement compared with original CNTs, were derived from corresponding literatures and summarized in Fig. 1. Oxide ceramics (including titanium oxide [4] and silicon oxide [5]) were usually coated onto CNTs via sol–gel approach, and could not sufficiently defend CNTs from oxidation. Carbide ceramic (including SiC [6,7] and SiOC [8,9]) coatings could be generated onto CNTs via solution phase [8,9] or solid phase [6,7] reactions, and the compact ceramic coatings provided CNTs with enhanced oxidation resistance. However, carbides tend to be oxidized at high temperature [17], limiting the protecting effect. On the contrary, nitride ceramics were rather stable in oxidizing atmosphere, even at 1000 °C [17]. Nitride ceramics, such as SiCN [10], Si(B)CN [11], SiAlCN [12] and BN [14,16], have been successfully coated onto CNTs; and the compact, stable ceramic coating could provide CNTs with relatively better anti-oxidation performance.

Aluminium nitride (AlN) is a nitride ceramic which can generate thin but compact oxide layer and be stable in oxygen until 1077 °C, and widely used in the industries [17]. This unique chemical structure

can be applied to effective anti-oxidation coating, but it's pity that no such protection was accomplished onto CNT surface. Liu and co-workers fabricated AlN nanowires by using CNTs as template and Al, Al₂O₃ and NH₃ as reactants [18,19]. Tailleux and co-workers coated CNT array with AlN by using chemical vapor deposition method, and cauliflower-like structure was achieved [20]. Despite the advantage of AlN in anti-oxidation, proper coating structure should be constructed onto CNT surface to utilize the oxidation resistance.

In the present study, a facile strategy for coating CNTs with AlN was developed. CNTs were coated with ceramic precursor via gradual sedimentation in a mixed solution of isopropanol and toluene, the subsequent pyrolysis and carbothermal reduction nitridation generated AlN layer on the nanotube surface. Thermogravimetric analysis (TGA) was performed to evaluate the oxidation resistance of CNTs coated with AlN. Furthermore, the coating mechanism was proposed and discussed.

2. Experimental procedure

Multi-wall carbon nanotubes were obtained from Chengdu Organic Chemicals Co., Ltd (Chengdu, China). They were produced by chemical vapor decomposition method, with an outer diameter in the range of 20–30 nm, and a length in the range of 5–10 μm. Polyalumoxane (PAO) was produced in our lab by following a previously reported method [21], and used as aluminium-containing precursor. The general synthesis evolved controlled hydrolysis of aluminium isopropoxide and condensation polymerization. The as-produced PAO was soluble in isopropanol and ethanol, partially soluble in toluene and acetone. Allyl novalac resin (ANR) was purchased from Shengquan Group Co., Ltd

* Corresponding authors.

E-mail addresses: yeli@iccas.ac.cn (L. Ye), tzhao@iccas.ac.cn (T. Zhao).

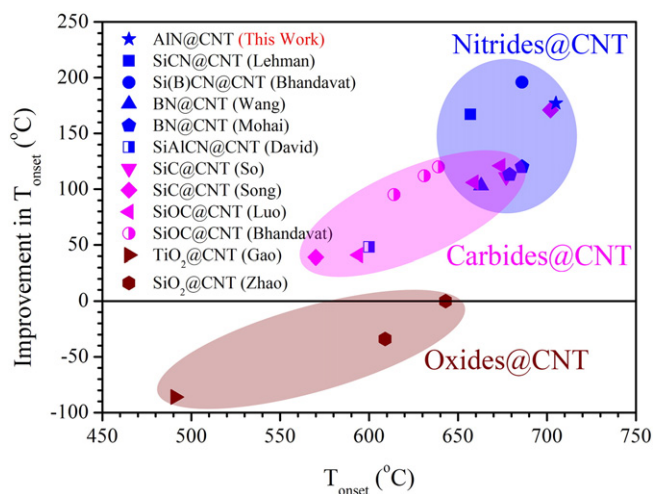


Fig. 1. Comparison of onset oxidation temperature (T_{onset}) and the improvement compared with original CNTs of different ceramic coated CNTs. The data were derived from corresponding literatures and might contain minor errors.

(Jinan, China), and used as the carbon source. The as-received ANR was soluble in toluene and acetone, but insoluble in isopropanol and ethanol. Isopropanol, ethanol, toluene and acetone were all analytical reagents and used as received.

For preparing CNTs coated with AlN of 1 nm in thickness, 1.0 g of CNTs, 1.07 g of PAO and 0.21 g of ANR were dispersed into 100 ml of isopropanol and 20 ml of toluene with mechanical agitation. Upon stirring for 15 min, the mixture was treated with tip ultrasonication for 30 min to achieve a homogenous dispersion. Then the mixture was gently heated to and held at 70 °C, allowing the solvent to slowly but completely evaporate. After that, the dried black powder was cured at 200 °C for 2 h and pyrolyzed at 800 °C for 2 h, under flowing nitrogen. Then the sample was transferred to a graphite furnace and treated at 1550 °C for 2 h and 1700 °C for 2 h, under flowing nitrogen. The heating and cooling rates were both 4 °C/min. Finally, the sample was placed into an air oven and treated at 650 °C for 0.5 h to remove any pyrolysis carbon residual. Here, we designated the obtained product as AlN@CNT, and the general procedure was illustrated in Fig. 2.

Based on the above method, AlN@CNT with different coating thickness could be prepared, only by altering the proportion between CNTs, PAO and ANR. The proportions for fabricating AlN@CNT with coating thickness of 2, 3 and 5 nm were 1:2.23:0.46, 1:3.46:0.69 and 1:6.19:1.24, respectively. The corresponding products were designated as AlN@CNT-x nm, where x represented the coating thickness.

Scanning electron microscope (SEM) analysis was carried out on a Hitachi S-4800 microscope with an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDX) was performed on an Oxford

INCAx-sight 7593 system linked to the SEM. Transmission electron microscope (TEM) analysis was carried out on a JEOL JEM-2100F microscope with an accelerating voltage of 200 kV. The phase evolution was characterized by using a Rigaku D/max 2500 powder X-ray diffractometer. TGA tests were performed on a Netzsch STA 409PC instrument. Samples weighing ~8 mg were heated from 25 to 1000 °C at a rate of 10 °C/min, in air flowing at 50 ml/min. Raman spectroscopy (Renishaw inVia plus; $\lambda = 532$ nm) was performed to investigate the crystal nature of the product.

3. Results and discussion

Given the diameter of CNTs and the density of CNTs and AlN, the coating thickness can be adjusted by altering the proportion between CNTs and aluminium-containing precursor. Here, the coating thickness was designed to be ~1 nm, and detailed characterization was conducted to investigate the coating. SEM images in Fig. 3(a) showed that the product had smooth, stick-like morphology, which was similar to that of pristine CNTs. Besides, the inset digital camera image showed that the product was in black color. EDX spectrum in Fig. 3(b) revealed the presence of C, N and Al within the structure, with atomic ratio close to the designed structure. The tiny oxygen presence might be a result of the minor oxidation of the AlN coating. Fig. 3(c) showed typical XRD patterns of pristine CNTs and AlN@CNT. Peaks labeled in the spectrum can be indexed to hexagonal AlN crystal with lattice parameters of $a = 3.114$ Å and $c = 4.986$ Å (JCPDS Card No. 08-0262). Besides, (002), (100) diffraction peaks for CNTs were also observable in the figure. The low magnification TEM image in Fig. 3(d) revealed the hollow, tube-like morphology of AlN@CNT. Fig. 3(e, f) displayed high resolution TEM images of the product, parallel tube walls and AlN crystalline region could be clearly identified and were labeled on the figure. The coating was approximately 1 nm in thickness, closely attached onto the tube walls and defect free. Besides, the AlN crystals tended to be randomly oriented. From the above characterization, it could be concluded that the CNTs were coated with AlN as designed.

Moreover, AlN@CNTs with different coating thickness were also prepared and characterized for understanding the coating strategy better. SEM image in Fig. 4(a) revealed that AlN@CNT-2 nm possessed smooth, stick-like morphology, which is similar to AlN@CNT-1 nm. And TEM image in Fig. 4(b) further confirmed that the coating thickness was approximately 2 nm, closely as designed. However, when the coating thickness was more than 3 nm, the obtained ceramic layer might be somehow imperfect. SEM image in Fig. 4(c) and TEM image in Fig. 4(d) both revealed that the coating layer of AlN@CNT-3 nm was not uniform in thickness. While the thickness was 5 nm, the heterogeneity of AlN@CNT-5 nm exacerbated; flake-like particles, which might be individually grown AlN ceramic, could be identified in Fig. 4(e). Finally, XRD spectrum was used to evaluate the phase structure of AlN@CNT with different coating thickness; all characteristic peaks for both AlN

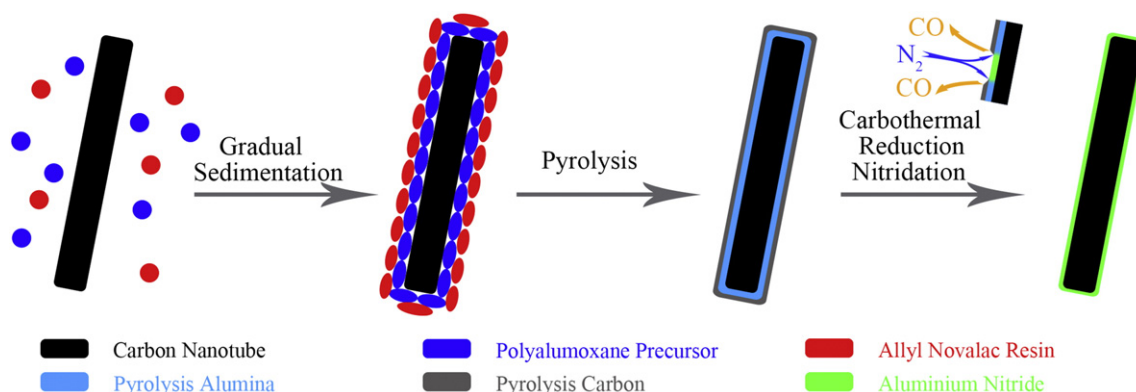


Fig. 2. Strategy for coating CNTs with AlN.

Download English Version:

<https://daneshyari.com/en/article/1657009>

Download Persian Version:

<https://daneshyari.com/article/1657009>

[Daneshyari.com](https://daneshyari.com)