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Chinese ink-facilitated fabrication of carbon nanotube/polyvinyl alcohol composite sheets with a high nanotube loading

W.L. Yan, A. Dasari, L.B. Kong *

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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ABSTRACT

Fabricating carbon nanotube-based composites requires high degree of dispersion of carbon nanotubes into a polymer matrix. The widely used approaches reported in open literature for such a purpose are usually complicated and high-cost. Herein, we found that Chinese ink could be used to prepare composites composed of multi-walled carbon nanotubes (MWCNTs) and polyvinyl alcohol (PVA). The Chinese ink acted as a solvent and a dispersant. The MWCNT-ink-PVA ternary composite possessed both high flexibility and high electrical conductivity, with an optimized electrical conductivity of 8.17 S cm^{-1}. This simple method is believed to be applicable to other nanosacle carbon materials.

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention in recent years [1]. CNTs are regarded as promising building blocks for high-performance materials and devices because they demonstrate excellent mechanical properties [2,3], high aspect ratio [4] and exceptional thermal [5,6] and electrical conductivities [7]. To realize this potential on a macroscopic scale, individual CNTs should be translated into large-size assemblies, such as one-dimension fibers [8–10], two-dimension films or sheets [11,12] and three-dimension bulks [13,14].

However, a huge challenge still lies in materializing this process. Because of their high aspect ratio and inert surface, pristine CNTs have poor interfacial interaction with both aqueous and organic solvents, resulting in an inherent difficulty in dispersing them in liquid media [15]. Surface functionalization and the use of surfactant supported by sonication are general ways to solve this problem [15–17]. Most of these methods have ineluctable shortcomings, such as high cost, high risk and low efficiency. Furthermore, fabrication of CNT/polymer composites with high CNT content is also a difficult task. Therefore, developing a low-cost and simple method to utilize CNTs in on a practicable scale is always desirable.

Chinese ink has been extensively used as a black pigment in calligraphy and Chinese ink wash drawings for two millennia. It has unique physical and chemical properties that endow it with endurance among artists' materials. Essentially, Chinese ink is an intimate mixture of carbon particles, glue and miscellaneous additives [18,19]. The carbon particles used in Chinese ink can be generally divided into two types: soot and lampblack, which are respectively the products of incomplete combustion of pinewood and oil lamp (such as tung oil and rapeseed oil) [20–22]. Both soot and lampblack are almost spherical in shape with primary particle sizes ranging from 10 to 150 nm, whereas the lampblack tend to be smaller in size and narrower in size distribution when compared with soot [18]. Unlike commercial carbon black produced in well-controlled conditions, soot and lampblack have a low purity of carbon and a considerable variation in particle shape and size [23]. They may fuse or aggregate to form large-sized clusters. The glue, animal glue (such as hide glue and egg white) and/or plant gum (such as Arabic gum, fruit tree gum, starch and honey), is used as a dispersant to enhance dispersion of the carbon particles in water and as binders to avoid the fracture of inksticks-solid-state Chinese ink [19,24,25]. The presence of glue changes the surface chemistry of carbon particles and stabilizes them in aqueous suspensions [18]. The additives, normally perfumes and herb extracts, are added to improve physical properties of Chinese inks, such as odor, tint and appearance.

Although there have been researches on identification of their ingredients [18,19,22,24–28], commercial Chinese ink has rarely been used as a raw material in scientific research. However, in this article, we developed a simple method to fabricate CNT-based composites by using commercial Chinese ink as a raw material. It was found that pristine multi-walled carbon nanotubes (MWCNTs) could be directly dispersed into Chinese ink without using any

* Corresponding author. Tel.: +65 67905032; fax: +65 67909081.
E-mail address: elbkong@ntu.edu.sg (L.B. Kong).

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surfactant. The suspension of Chinese ink and MWCNTs could be readily incorporated with polyvinyl alcohol (PVA) that served as a polymer matrix. In a very simple way, MWCNT-ink-PVA ternary composite sheets were fabricated by wet-casting and air-drying the suspensions. It allowed us to fabricate composites with high concentrations of MWCNTs, which is still a challenge. The composites possessed both high electrical conductivity and high flexibility. We believe that such a simple and scalable method can be applicable to other nanoscale carbon materials, such as carbon nanofibers and graphene nanosheets.

2. Experimental

2.1. Materials

A lampblack-type Chinese ink was purchased from Sino-Japanese joint venture, Anhui Hongxing ink Co. Ltd. This Chinese ink is very homogeneous without obvious coagula. MWCNTs, produced by chemical vapor deposition, with an average length of ~50 μm and diameters ranging from 8 to 15 nm were supplied by Timesnano (Chendu Organic Chemicals, China). PVA powder ($M_w \sim 70{,}000–100{,}000$, Aldrich) was dissolved into deionized water at 80 °C and stirred for 4 h to obtain clear PVA solutions with concentrations of 1.0, 2.5 and 5.0 wt%. All chemicals and the Chinese ink were used as received without any purification or pretreatment.

2.2. Composite preparation

In a typical procedure, 2.0 g of Chinese ink and up to 0.10 g of pristine MWCNTs were first mixed in an agate mortar by manual pestle-milling. In fact, the MWCNT loading content can be even higher. After the MWCNTs and Chinese ink were thoroughly mixed, up to 5.0 g of PVA solution with a concentration of 1.0 wt%, 2.5 wt% or 5.0 wt% was added. The mixtures were kept milling and stirring until they became smooth. These resulting viscous suspensions were then cast onto a glass or plastic (polystyrene) petri dish with a diameter of 50 mm, where they were left to air-dry at room temperature. The time needed to air-dry a suspension may vary from 24 to 72 h, depending on the amount used. Finally, the air-dried free-standing MWCNT-ink-PVA ternary composites were peeled off from the glass or plastic dish. For comparison, pure PVA sheets and binary composites without MWCNTs, ink or PVA were prepared in the same way. For tension test, because the standard specimen cutter had an overall length of 63.5 mm, the samples should have larger sizes to meet the dimensional requirements. Thus, we doubled the amount of each component to give sufficient volume of suspensions and used petri dishes with a diameter of 80 mm for suspension casting.

2.3. Characterization

Field-emission scanning electron microscopy (FESEM; JEOL-6340F, operated at 5.0 kV accelerating voltage) was applied to examine the surface and cross-section morphology of the prepared composites. Due to the low electrical conductivity, the MWCNT–PVA and ink-PVA binary composites were coated with platinum with a thickness of about 5 nm beforehand to avoid surface charging during examination.

Thermo-gravimetric analysis (TGA; TA Instruments, Model Q500) was performed to investigate the component content of the used Chinese ink and the composites. The analysis was conducted in a platinum pan from room temperature to 600 °C at a heating rate of 20 °C· min^{-1} in nitrogen atmosphere.

A tension tester (Instron, Model 5567) was used to measure Young's modulus, tensile strength and elongation at break of the composites. All the testing samples were cut by a standard dumbbell-shape cutter with dimensions in line with ASTM D638-Type V. A lab micrometer (Mitutoyo) was used to measure the thickness of the samples in triplicate, which usually ranged from 0.2 to 0.4 mm. The test method for such thin sheet samples followed the standards in ASTM D882 (as shown in Table 1). The initial distance between grips was set to be 25.4 mm. An initial strain rate of 10.0 mm/mm min was applied since the elongation at break of both pure PVA and PVA-contained composites was larger than 100%. For each group of the composite, 8–10 specimens were tested to obtain an average value.

An automatic mapping four point probe system (Materials Development Corporation, Model CMT-SR2000N) was employed to measure electrical conductivity of the composites at room temperature. A glass slide was used as a substrate since the sheets were so thin that the probe can penetrate them and give false results. For each sample, 9 even-distributed points were tested to get an average value.

3. Results and discussion

3.1. Morphology of the composites

Freestanding MWCNT-ink-PVA composite sheets can be easily fabricated by wet-casting the three-component suspensions with appropriate compositions. Here, the commercial Chinese ink acts as a liquid vehicle and a dispersant for the dispersion of MWCNTs [29]; it can be readily incorporated with a PVA solution since it is water-based.

Due to the poor interaction between CNTs and polymers, uniformly dispersing CNTs into a polymer matrix remains a great challenge [30,31]. Surface modification of CNTs [32,33] and/or the usage of surfactants with a support of sonication [29,34,35] are commonly required to improve CNT–polymer matrix wetting and adhesion. However, the approaches are either complicated or high-cost and thus unsuitable for production on a large scale. Besides, it is difficult to fabricate homogeneous composites with high CNT content by using these methods. In contrast, our approach is straightforward, by which composites with high CNT concentration can be readily fabricated.

Typical appearance of the as-prepared MWCNT-ink-PVA composites is demonstrated in Fig. 1. Depending on the total amount of MWCNTs, ink and PVA, the thickness of these sheets ranges from 0.2 to 0.4 mm. These air-dried composite sheets showed high pliability. They can revert to their original appearance in a short time even after being rolled into cylinder-shape (as shown in Fig. 1(c)). By changing the amount of a suspension and the dimensions of a substrate, the composite sheets can be made in any size and thickness.

Representative FE-SEM images of the as-prepared MWCNTs-ink-PVA ternary composites are shown in Fig. 2(a–d). For comparison, the images of MWCNT–PVA (Fig. 2(e and f)) and ink-PVA (Fig. 2(g and h)) binary composites are also presented. As seen in the low-magnification image (Fig. 2(a and c)), MWCNTs, surrounded by the lampblack particles (LBPs) from the Chinese ink, are well dispersed within the composite. The high-magnification images (Fig. 2(b and d)) provide an insight into the arrangement of MWCNTs and LBPs. These spherical-shaped LBPs, with a diameter close to the outer diameter of the MWCNTs, are found to be inserted into the space between adjacent MWCNTs, leading to the separation of MWCNTs. It is seen from the cross-sectional view that, the MWCNTs seem to form a framework for the "bricks" – the dispersive LBPs, which in return support the framework. Meanwhile, PVA functions as a binder to hold these MWCNTs and LBPs together to form a cohesive composite sheet. However, without the presence of LBPs (Fig. 2(e and f)), the entangled MWCNTs tend to aggregate,