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

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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 $8.17 \text{ S}\cdot\text{cm}^{-1}$. This simple method is believed to be applicable to other nanoscale carbon materials.

Keywords: Carbon nanotubes, Flexible composite, Freestanding composite, Chinese ink

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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, rapeseed oil, etc.) [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, egg white, etc.) and/or plant gum (such as Arabic gum, fruit tree gum, starch, honey, etc.), is used as dispersants 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 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 ($M_w \sim 70,000\text{-}100,000$, 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 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 to 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, f)) and ink-PVA (Fig. 2 (g, h)) binary composites are also presented. As seen in the low-magnification image (Fig. 2 (a, 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, 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, f)), the entangled MWCNTs tend to aggregate, resulting in the non-uniform distribution within the PVA matrix; while in the absence of MWCNTs (Fig. 2 (g, h)), the LBPs are tightly bound together by PVA, forming a condensed cake. These FE-SEM images clearly demonstrate that the MWCNTs and the LBPs from Chinese ink mutually promote the distribution of each other within the composite.

It is necessary to mention that thorough mixing and slow drying are necessary to prepare composites without visible pores or cracks. Chinese ink-assisted milling can help to break the MWCNT bundles and to produce more contact surface with PVA. Moreover, as stated above, carbon nanoparticles (LBPs) can be stabilized in Chinese ink with the action of glue and the other additives. As such, MWCNTs can be dispersed in Chinese ink. During milling, MWCNTs would be dispersed in the Chinese ink-PVA mixture and have more interfacial interaction with PVA. Thus, the resulting composites are expected to have good mechanical properties [36]. On

the other hand, the drying rate of the cast suspension is also a key factor affecting composite appearance. We found that air-drying under the ambient conditions (25°C and about 50% of humidity) is preferable. During the air-drying process, the water interchange between the composite and the air would eventually reach equilibrium. Therefore, the ambient humidity and temperature determined the moisture content and thus the flexibility of the as-prepared composite sheet [37]. Rapid drying usually causes severe shrinkage and even cracking on the composite sheets [38], especially for the samples containing relatively low contents of PVA.

3.2. Effects of Chinese ink

Chinese ink is an ancient and widely available commercial product. As described earlier, it has complex ingredients. Generally, Chinese ink contains nearly 90 wt% of water and 10 wt% of dry matters including lampblack/soot particles as major components, and glue (animal glue and/or vegetable gelatin) and miscellaneous additives as minor components. According to FE-SEM image (Fig. 2 (b)), the LBPs are spherical in shape with a diameter close to the outer diameter of MWCNTs. They may be broken into smaller particles or aggregated into clusters during the milling and drying [18].

To determine the carbon content of Chinese ink, we the raw Chinese ink was first naturally dried at room temperature to remove the free water. The dry matter content, W_1 , was calculated according to weight change. Then, these dry matters were subjected to TGA, heated from room temperature to 600°C at a heating rate of 20°C·min⁻¹, as shown in Fig. 3. The immobile water, glue and the other additives were removed at this step. The residue rate at 600°C, W_2 , was obtained. The approximate carbon content, W_c , was calculated by multiplying W_1 with W_2 . For the Chinese ink used in this study, W_1 was 6.86% and W_2 was 54.08%, so the calculated W_c was 3.71%. Admittedly, the ashes of glue and additives also make up a certain portion of the

residue at 600 °C. But since the ashes were much less than the lampblack, we ignored them during calculation.

The role of the Chinese ink could be summarized in two aspects. On the one hand, the dispersion of the MWCNTs was similar to that of the LBPs in the Chinese ink. During the mill-mixing process, the MWCNT agglomerates were broken by the shear force and the adsorption of the Chinese ink [39, 40, 41]. Meanwhile, the introduction of PVA increased the viscosity of the suspension, thus preventing the MWCNTs and LBPs from rapid settlement. As a result, a metastable MWCNT-ink-PVA suspension could be obtained. To check the stability, one as-prepared suspension containing 2.0 g of ink, 0.05 g of MWCNTs and 5.0 g of 2.5 wt%-PVA solution was kept in a sealed bottle and left alone. It was found that even after 72 h, no obvious sediments were found at the bottom. To further verify this, the dry matter content of the upper and the bottom suspension were analyzed by using TGA. There was almost no remarkable difference in the residual rate at 600°C between these two suspensions.

On the other hand, LBPs served as nanoscale spacers to prevent the MWCNTs from severe re-aggregating during the air-drying process. The evaporation of water caused a decrease in volume of the suspension, diminishing the motion space for LBPs and MWCNTs. When the volume decreased to a certain level, the dispersive LBPs and MWCNTs began to settle down in synchrony. The synchronous sedimentation made the LBPs and MWCNTs to be inter-lapped, preventing the MWCNTs from agglomerating. As a result, both the LBPs and MWCNTs were evenly distributed within the PVA matrix. Evidence to support this explanation can be found in the SEM images of Fig. 2 (b, d), where the MWCNTs and LBPs showed a “framework-brick” arrangement.

3.3. Properties of the MWCNT-ink-PVA composite

3.3.1. TGA analysis

Fig. 3 shows TGA profiles of pristine MWCNTs, pure PVA powders, raw liquid Chinese ink, air-dried (25°C) Chinese ink and an as-prepared composite. The TGA curve of the pristine MWCNTs exhibits negligible weight loss up to 600°C, confirming its high purity and thermal stability under nitrogen atmosphere [42]. In the curve of raw liquid Chinese ink, the distinct weight loss (~ 92%) at about 100°C is due to the evaporation of water and low-boiling-point materials, while the small weight loss step at about 300°C is attributed to the decomposition of some high-boiling-point materials, which indicates that the amount of the glues and additives used in Chinese ink is very low. The residual at 600°C mainly comprises LBPs. There are two weight loss stages in the curve of pure PVA. The weight losses at around 375°C and 450°C correspond to the decomposition of side chains and main chains of PVA, respectively [43].

The curve of the as-prepared composite has three regions: below 150°C, 150-500°C and above 500°C. The first region with weight loss of 15 wt%, occurring from room temperature to 150°C, is mainly due to the evaporation of moisture in the air-dried composite. The volatilization of some low-boiling-point materials used in the Chinese ink can also contribute to the weight loss in this region. In the second region, occurring at 150-500°C, the curve follows the trend of pure PVA, proving that the approximate 43 wt% of weight loss in this region is mainly ascribed to the thermal decomposition of PVA. In the third region, where the temperature is above 500°C, the curve levels off, indicating that after removing the polymers, the composite can be thermally stable in the nitrogen atmosphere. The residual rate of this composite is about 42%, which is very close to the theoretic value of 46%.

3.3.2. Mechanical properties

As shown earlier in Fig. 1, the as-prepared MWCNT-ink-PVA composite sheets possess high flexibility; they can be easily rolled or folded at a large angle and rapidly return to their origin shapes without any cracks. The good mechanical properties are mainly attributed to the presence of PVA. By contrast, although composite sheets can be fabricated without PVA, they usually have a loose structure, consisting of many visible pores or cracks, and thus are mechanically weak.

In general, the flexibility of the as-prepared composite sheets mainly depends on (i) the loading ratio of PVA to the sum of MWCNTs and LBPs, (ii) the moisture content of sheets and (iii) the degree of mixing of starting materials. It is well expected that more PVA and more moisture in the composite sheets, more flexible the composites would be. High degree of mixing contributes to the good interaction between the PVA matrix and the MWCNTs/LBPs, minimizing the number of possible weak points.

The results of tension test and the representative stress-strain curves are shown in Table 2 and Fig. 4, respectively. Compared to the pure PVA sheet and the ink-PVA binary composite sheet, the MWCNT-ink-PVA composite sheet possesses lower tension strength and lower elongation at break, but higher Young's modulus. CNTs are proved to be ideal reinforcements for polymers, since they possess excellent mechanical properties and high aspect ratio, especially SWCNTs [36, 44, 45]. As reinforcements, CNTs are usually used at relatively low concentrations. However, for the example in Table 2, the content of MWCNTs and LBPs is much higher than that reported in literature. Given the lampblack content in Chinese ink is 3.71%, then MWCNTs and LBPs account for about 20.0 wt% and 29.8 wt%, respectively. Such high content of MWCNTs and LBPs are unfavorable for force transfer within the composite sheet, because the deficiency of polymer matrix inevitably leads to the presence of weak points-

micro voids or pores that can be found in Fig. 2 (b, d) [44]. Even so, MWCNTs can improve the crystallinity of PVA so that the Young's modulus of composite sheet is increased [46]. MWCNT-ink-PVA composite sheets with such mechanical properties are acceptable if they are used as functional materials, which rely more on electrical and thermal conductivities [30].

3.3.3. Electrical conductivity

The electrical conductivity of a composite sheet is essentially dependent on the conducting network within the polymer matrix. The high aspect ratio and high electrical conductivity make CNTs ideal candidates for preparing conductive composites. In addition to CNTs, carbon black powders are also proved to be good conductive fillers for conductive composites [47, 48]. Like CNTs, they can construct a conductive pathway in a polymer matrix. In our method, Chinese ink contributed LBPs into the composite as conductive fillers.

It is worth noting that the electrical conductivity of a composite sheet is also significantly influenced by its moisture content. Since water-soluble PVA and the materials in the Chinese ink (such as glue and LBPs) can easily absorb water from the air, the as-prepared composite sheets always contain a certain amount of moisture that has a positive effect on flexibility but a negative effect on electrical conductivity. Thus, secondary drying is necessary in order to remove the moisture.

Table 3 summarizes the change in the thickness and the electrical conductivity of three composite sheets before and after secondary drying that was conducted at 50°C with air-blowing for 8 h. It is observed that after secondary drying, there is not much change in thickness, but a notable improvement in electrical conductivity. As a result, the electrical conductivity of the secondary dried composite sheets made from 1.0, 2.5, and 5.0 wt% PVA solutions change from 2.23, 4.84 and 1.91 $\text{S}\cdot\text{cm}^{-1}$ to 3.84, 8.17 and 3.39 $\text{S}\cdot\text{cm}^{-1}$, respectively. However, the conditions

of secondary drying should be well controlled to reach a compromise between mechanical strength and electrical conductivity. If dried excessively, the sheets would shrink and become fragile. Fragile samples cannot be tested by using the four-point probe instrument. For this reason, in this report, the temperature and the time of secondary drying conditions were set at 50°C and 8 h, respectively.

Table 4 compares the electrical conductivity of the MWCNT-ink-PVA ternary composite and three binary composites. It is noticed that there is a synergistic improvement in the electrical conductivity of the MWCNT-ink-PVA ternary composite, which exhibits higher electrical conductivity than the binary composites containing no MWCNTs, ink or PVA. Unexpectedly, the MWCNT-ink binary composite without an insulating polymer has a lower conductivity than the ternary composite, which can be attributed to its loose structure that not only makes the composite sheet easy to break, but also impairs the interaction between MWCNTs and LBPs. In this respect, PVA is necessary to maintain a conductive network. It is noteworthy that the ink-PVA composite shows higher electrical conductivity than the MWCNT-PVA composite, even though its LBP content is less than the MWCNT content of the MWCNT-PVA composite. This indicates that, besides the carbon (either LBP or MWCNT) content, the way how a conducting pathway is built in the composite also affects its electrical conductivity. Under the same preparation conditions, the spherical LBPs in Chinese ink are easier than entangled MWCNT bundles to be dispersed in PVA matrix, so they can form a smooth conducting network that guarantees the sheet conductivity.

The observed synergistic improvement in the electrical conductivity of the MWCNT-ink-PVA ternary composites can be attributed to the interaction between MWCNTs and LBPs. During the air-drying process, as the MWCNTs and the LBPs settled down simultaneously

without any disturbance, a conducting network was gradually formed. As discussed earlier, the MWCNTs constructed the main framework, whilst the conductive LBPs infilled the space between MWCNTs and supported the MWCNT framework. These LBPs increased the connecting points of the conducting network with PVA, promoting the interaction between the PVA matrix and the conducting network and guaranteeing the high conductivity. This is particularly useful when the sheet is subjected to mechanical deformation. We found that after the sheet was stretched or bent, the change in electrical conductivity was not significant.

Fig. 5 shows the electrical conductivity of the samples made from different PVA solutions as a function of MWCNT loading. As expected, the electrical conductivity of these ternary composites increases with increasing MWCNT content, especially from 0 to 0.02 g, and decreases with increasing PVA content. However, one exception is observed. When the MWCNT content is between 0.08 to 0.10 g, the sample made from 2.5 wt% PVA shows higher conductivity than the one made from 1.0 wt% PVA. As discussed above, though PVA is insulated, its presence is helpful in maintaining a conducting framework, especially when the MWCNT content is high. Therefore, with a certain amount of Chinese ink, there should be an optimum content ratio of MWCNTs to PVA, at which the composite sheet can demonstrate the highest conductivity with appropriate mechanical strength.

Due to the presence of Chinese ink, the MWCNTs can be dispersed in PVA with a large concentration, which largely boosts the conductivity of the resulting composite. The highest measured conductivity of ternary composite comprised of 0.10 g of pristine MWCNT, 2.0 g of Chinese ink and 5.0 g of PVA solution (2.5 wt%) is $8.17 \text{ S}\cdot\text{cm}^{-1}$, which is comparable to the values reported in open literature [49, 50]. The high electrical conductivity makes the composites possible for various applications, such as electrode materials of energy storage devices and

electromagnetic shielding. Since the electrical conductivity of the composites is mainly contributed by the conductive components, further enhancement in conductivity is possible by using high quality CNTs or graphene nanosheets. It is strongly believed that this method is applicable to other nanoscale carbon materials, such as single-walled CNTs, graphene or graphene oxide and carbon nanofibers. Moreover, other components, such as noble metallic nanoparticles and oxide nanoparticles can be included to fabricate multi-functional composites. In addition, the precursors for the fabrication of the composites can be used as conductive inks in printing flexible electrodes and devices [51].

4. Conclusions

A simple and scalable method has been developed to fabricate CNT-based composites by using commercial Chinese ink as solvent and dispersant. The as-prepared MWCNT-ink-PVA ternary composites possessed high flexibility and electrical conductivity, with a maximum electrical conductivity of $8.17 \text{ S}\cdot\text{cm}^{-1}$. Compared with those methods widely reported in the literature, the method developed in this work has obvious advantages, including processing simplicity, cost-effectiveness and environmental friendliness. It is believed that this simple method should be applicable to fabricating composites with other nanosized carbons, such as carbon nanofibers and graphene nanosheets.

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Figure Captions

Fig. 1. Representative photographs of the as-prepared free-standing ink-MWCNT-PVA composite sheets: (a) relatively rough top surface, (b) smooth and somewhat reflective bottom surface and (c) recovery of rolled sample (0.10 g MWCNTs + 2.0 g Chinese ink + 5.0 g 2.5 wt% PVA solution).

Fig. 2. Representative FESEM images of the as-prepared composite sheets: (a-d) 0.10 g MWCNTs + 2.0 g ink + 5.0 g PVA (2.5 wt%), (e, f) 0.10 g MWCNTs + 5.0 g PVA (2.5 wt%) and (g, h) 2.0 g ink + 5.0 g PVA (2.5 wt%). (c, d) is cross-sectional image (torn by hand), while the others are vertical images.

Fig. 3. TGA curves of MWCNTs, pure PVA, raw liquid ink, air-dried (at 25°C) ink and the as-prepared composite consisting of 0.05 g MWCNTs, 2.0 g ink and 5.0 g PVA solution (2.5 wt%). All the samples were heated from room temperature to 600 °C at a heating rate 20°C·min⁻¹.

Fig. 4. Typical stress-strain curves of pure PVA sheet, ink-PVA composite sheet and MWCNT-ink-PVA composite sheets.

Fig. 5. Effects of the contents of MWCNT and PVA on conductivity of the composite sheets. For all samples, 2.0 g of Chinese ink and 5.0 g of PVA solution were used. The loading of PVA was controlled through the concentration (1.0 wt%, 2.5 wt% and 5.0 wt%). All samples were secondary dried at 50°C with air-blowing for 8 h before testing.

Table Captions:

Table 1 Standards for mechanical testing.

Table 2 Results of mechanical testing of different samples.

Table 3 Effect of drying (50°C, 8 h) on conductivity of the composite sheets ^a.

Table 4 Electrical conductivity of the MWCNT-ink-PVA ternary composite and the binary composite without either MWCNTs, ink or PVA.

Table 1 Standards for mechanical testing.

Standards	Items	Values
ASTM D638 (Type V)	Width of narrow section	3.18±0.03 mm
	Gage length	7.62±0.02 mm
	Length of narrow section	9.53±0.08 mm
	Length overall	63.5 mm
ASTM D882	Initial strain rate	10.0 mm/mm·min
	Initial distance between grips	25.4 mm
	Rate of grip separation (extension rate)	254 mm/min

Table 2 Results of mechanical testing of different samples.^a

Samples	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Pure PVA	35.3±9.2	41.6±3.2	902±36
10.0 g PVA (2.5 wt%)+4.0 g ink	34.7±3.9	19.3±1.4	524±27
10.0 g PVA (2.5 wt%)+4.0 g ink+0.10 g CNTs	66.7±8.6	16.8±1.4	205±14

^a Data are mean ± standard derivation (SD).Table 3 Effect of drying (50°C, 8 h) on conductivity of the composite sheets ^a.

Concentration of PVA solution (wt%)	Conductivity (S·cm ⁻¹)		Thickness (cm)		Change in Conductivity (%)	Change in thickness (%)
	Before drying	After drying	Before drying	After drying		
1.0	2.23	3.84	0.02358	0.02356	72.2	-0.08
2.5	4.84	8.17	0.02326	0.02294	68.8	-1.38
5.0	1.91	3.39	0.01668	0.01642	77.5	-1.56

^a All the samples contain 0.10 g of MWCNTs, 2.0 g of Chinese ink and 5.0 g of PVA solution with concentrations of 1.0 wt%, 2.5 wt% and 5.0 wt%, respectively.Table 4 Electrical conductivity of MWCNT-ink-PVA ternary composite and the binary composite without either MWCNTs, ink or PVA^a.

No.	MWCNTs (g)	Chinese ink (g)	2.5 wt% PVA solution (g)	Conductivity (S·cm ⁻¹)
1	–	2.0	5.0	0.80
2 ^b	0.10	–	5.0	0.61
3 ^b	0.10	2.0	–	3.40
4	0.10	2.0	5.0	5.07

^a All the samples were dried at 50 °C with air-blowing for 8 h before testing.^b These two samples were incompact in structure and hence easy to break.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.