Fabrication and characterization of multi-walled carbon nanotubes-based ink

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Since the discovery of carbon nanotubes in 1991 [1], they have been the targets of numerous investigations due to their unique properties [2, 3]. Recently, Carbon-based inks had gained increasing popularity in electronic packaging applications [4] and electrochemical sensors [5, 6], owing to their low cost, environmental compatibility, and lower assembly temperature [7]. For example, a small RF (Radio frequency) chip assembled onto a paper substrate having a printed carbon-ink antenna, was used to wirelessly transmit and receive information [8]. Recent studies demonstrated that CNT (Carbon nanotubes) based electrodes made by screen-printing [9] or hand-printing [10], had better electrochemical properties and analytical performance than that of graphite-based electrodes due to its high conductivity. If CNT-based ink could be printed by ink-jet printer, it may be convenient and precise to prepare conductive-coating layer. However, it is difficult to obtain stable CNTs suspension with uniform length, due to its special surface properties and entangled structure, since such unstable CNTs suspension always jams the printer nozzle. In this letter, stable inkjet-printable CNT-based ink was prepared by special method as described below, the relationship between manipulation parameters and the conductivity of printed CNTs strips on paper were also investigated.

The MWNTs (Multi-walled carbon nanotubes) samples used in this work were prepared by the catalytic decomposition of propylene on Fe/Al_2O_3 catalyst in a nano-agglomerated fluidized-bed reactor (NAFBR). Details of the catalyst and the CNT's preparation method were described elsewhere [11, 12]. MWNTs were purified and cut in a mixture of 3:1 H_2SO_4/HNO_3 at 140 °C for 30–60 min, and then filtrated and washed with de-ionized water to PH7. The suspension of MWNTs in water was centrifuged for 10 min at 3000 rpm and the deposit was taken out. Then, the residual suspension was continually centrifuged for 15 min at 20000 rpm, and subsequently the deposit was taken out and dispersed ultrasonically in distilled water with addition of some special dispersant (S27000, made in Japan) to prepare CNT-based ink (CNTs concentration is 0.1, 0.2, 0.3, and 0.4 wt.%, respectively). In this experiment, the diameter of the inkjet printer nozzle (resolution: 4800 × 1200 dpi, Lenovo Group) was less than 1 μm. The carbon strips (3 mm × 3 mm) and image were printed on paper using inkjet printer. The electrical resistance of strips (working area: 3 mm × 3 mm) printed on paper was measured by digital ohmmeter and digital insulation resistance tester (DY30-1) by putting parallel copper flakes on the strip tightly at room temperature. The surface was repeatedly rinsed with distilled water and dried 10 times in order to investigate the adhesion of CNTs to paper. The microstructures of samples were characterized by scanning electron microscopy (JEOL-6700F).

Fig. 1 shows the configuration of the as-grown MWNTs. It can be observed that the MWNTs agglomerate is made up of many sub-agglomerates (Fig. 1a) due to its special preparation method—catalytic chemical vapor deposition in a nano-agglomerate fluidized-bed reactor. Further SEM observation (Fig. 1b) shows that the single sub-agglomerate is randomly entangled

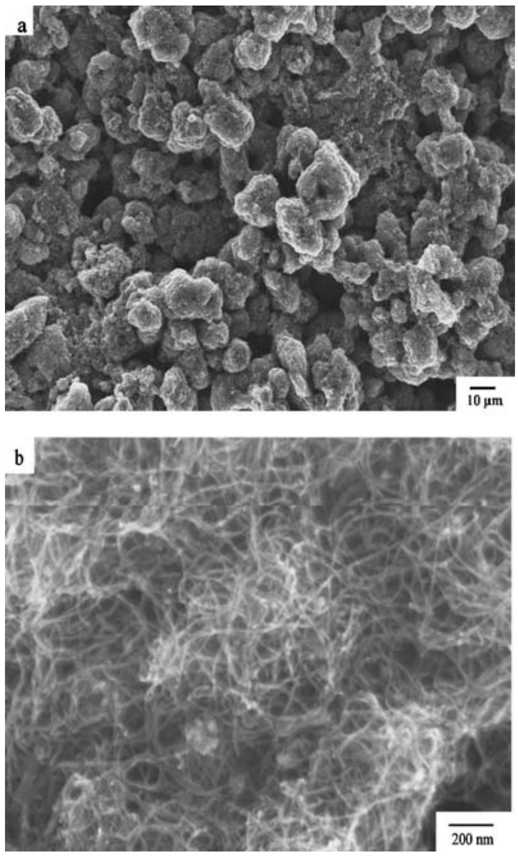

Figure 1 SEM images of the as-grown MWNTs.

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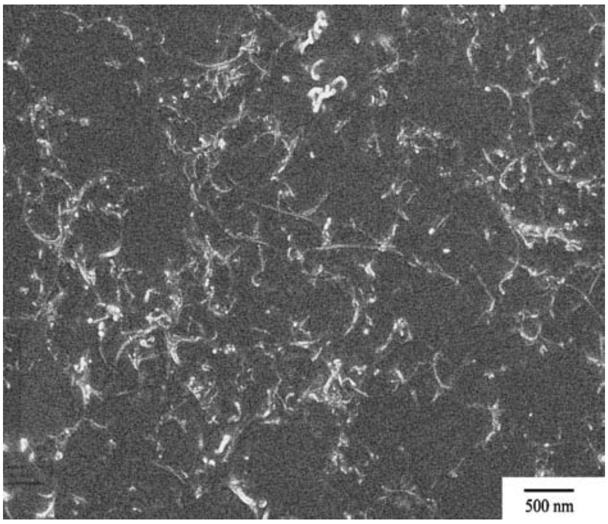

Figure 2 SEM image of MWNTs after treatment.

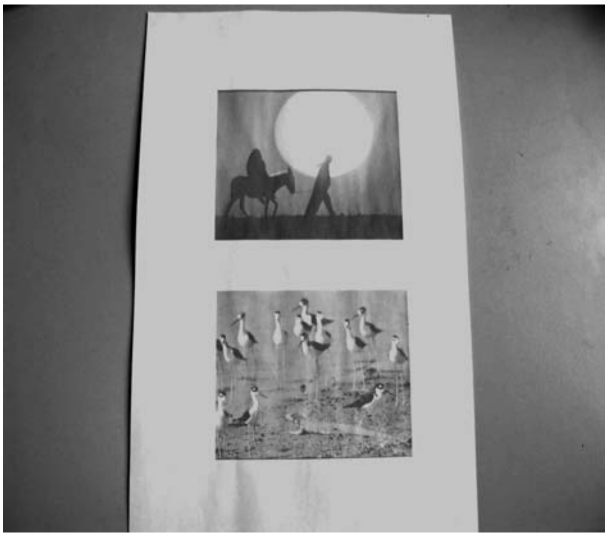

Figure 3 The printed picture on paper (MWNTs concentration: 0.3 wt.%).

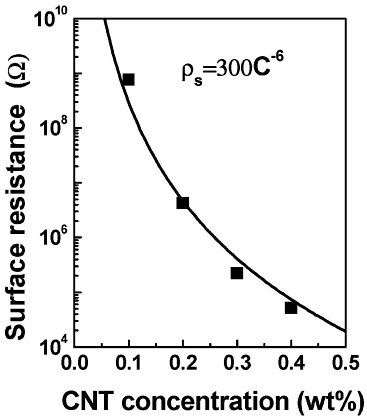

Figure 4 The relationship between the MWNTs concentration and the resistance of printed strips on paper.

and cross-linked, which make it difficult to measure the accurate length of the MWNTs except knowing the length of CNTs being more than several tens of micrometers.

Fig. 2 shows SEM image of MWNTs after acid treatment. MWNTs were cut much shorter (100 nm–10 μm) by chemical treatment, although the length of MWNTs is inhomogeneous due to the occurrence of chemical reaction in random active site. While MWNTs, with the length in a narrow range (400 nm–800 nm), can be effectively screened out by appropriate step-centrifuge method (as shown in Fig. 2), which can be stably dispersed in water with the addition of dispersant.

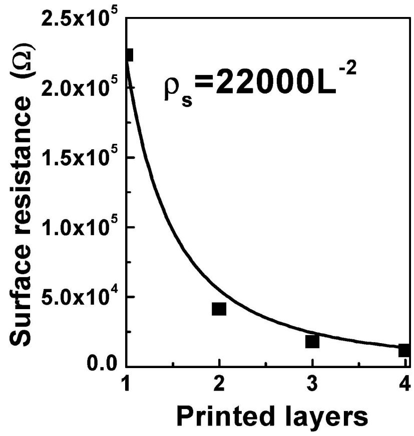

Figure 5 The relationship between the electrical resistance and the printing layers (MWNTs concentration: 0.3 wt.%).

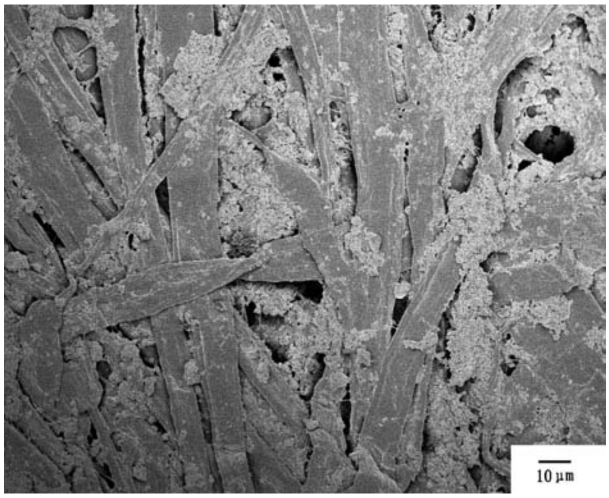

Figure 6 SEM image of blank paper.

Fig. 3 shows the printed picture on paper. Though MWNTs concentration is 0.3 wt.%, the picture has enough black degree and definition fitting for the requirement of printing due to MWNTs well dispersion on paper. In addition, the printed MWNTs surface remains rigid and stable after being rinsed several times with distilled water due to the strong Van der Waals surface tension between CNT and paper.

Fig. 4 shows the relationship between MWNTs concentration and resistance of printed strips on paper. The resistance of strip strongly depends on MWNTs concentration. With the increase in MWNT's concentration, the electrical resistance decreases in an exponent by $\rho = \kappa \times C^{-6}$(C presents MWNTs concentration). At the same time, the resistance also decreases with the addition of printed layers at the same MWNTs concentration (0.3 wt.%) as shown in Fig. 5. The electrical resistance decreases remarkably and then mildly, with the increase of printed layers. The decrease of resistance also accords with printed layers in an exponent by

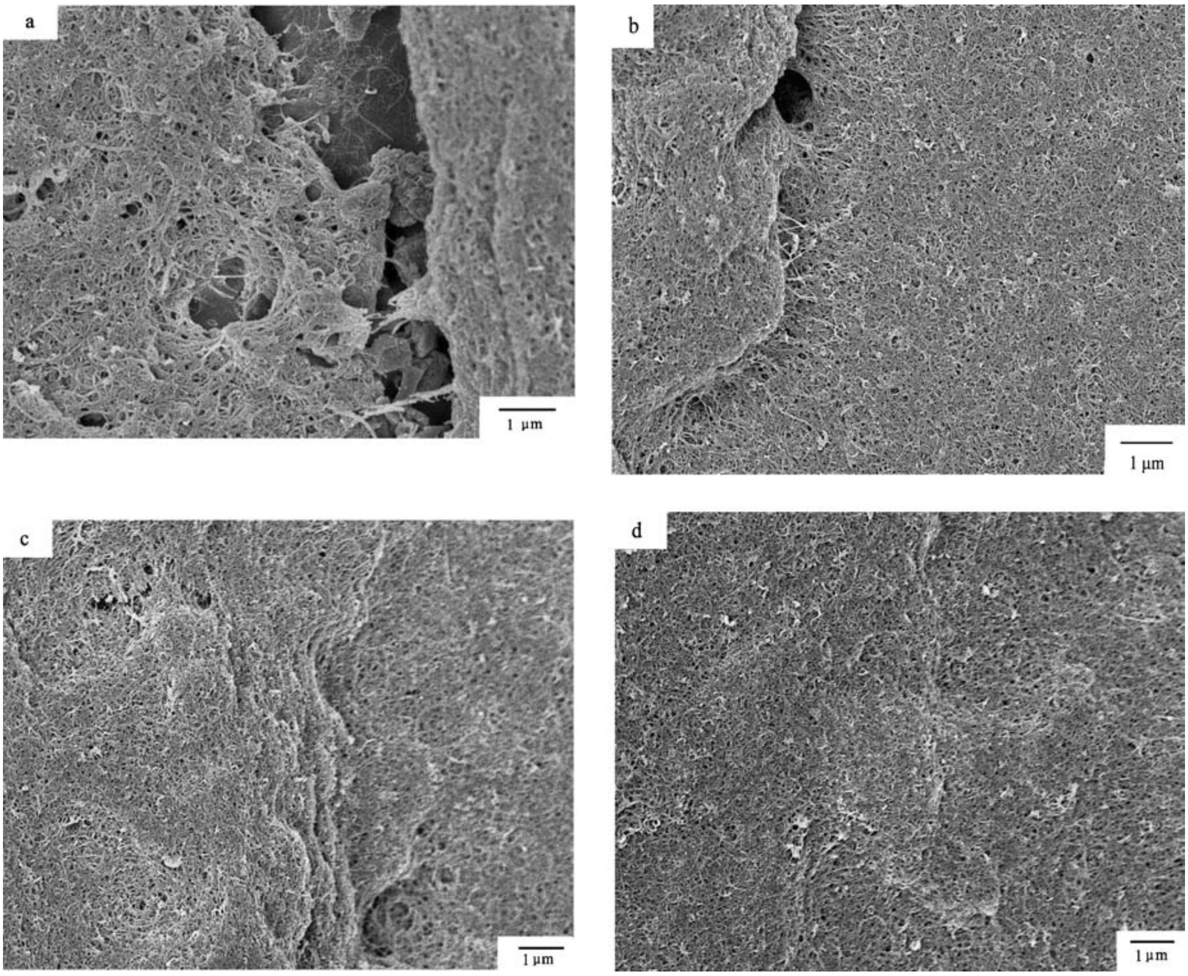

Figure 7 (a) SEM images of carbon stripe on paper (printed one layer) (b) SEM images of carbon stripe on paper (printed two layers) (c) SEM images of carbon stripe on paper (printed three layers), and (d) SEM images of carbon stripe on paper (printed four layers).

$\rho = \kappa \times L^{-2}$(L presents printed layer). When the strip is printed to four layers, the electrical resistance is only 11 600 Ω. Since, there are a lot of defects such as holes on the surface of blank paper as shown in Fig. 6, for the first printed layer, MWNTs cannot form good conductive network (Fig. 7a). With the increase of printed layers, continuous MWNTs conductive network were formed gradually, which effectively decreased the electrical resistance of the strips (Fig. 7b, c and d). When the strip is printed to three layers, the network is compact and consecutive enough to cover almost all holes and voids on the paper, so the electrical resistance of the strips hardly decreases with the increase of printing times.

In conclusion, stable CNT-based ink has been successfully prepared and printed on paper. The printed samples, not only have excellent black degree, definition, and electrical properties, but also possess excellent adhesion to paper. With the increase in MWNT's concentration and printed layer, the electrical resistance of printed strip decreases in an exponent form. Therefore, it is possible to coat highly conductive CNTs layer on some other substrates by ink-jet printer with easy and precise control.

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