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Abstract

The inkjet processing of water dispersable polymer carbon nanotube composite materials is reported. Single printed layers displayed good optical transparency, sheet resistance, and conductivity. It is demonstrated that an alcohol sensor based on a single printed layer of polymer carbon nanotube composite could operate at a lower voltage compared to a sensor based on a single printed layer of the polymer.

Keywords

Inkjet, printing, viable, tool, for, processing, polymer, carbon, nanotube, composites

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Inkjet printing: a viable tool for processing polymer carbon nanotube composites

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ABSTRACT

The inkjet processing of water dispersable polymer carbon nanotube composite materials is reported. Single printed layers displayed good optical transparency, sheet resistance, and conductivity. It is demonstrated that an alcohol sensor based on a single printed layer of polymer carbon nanotube composite could operate at a lower voltage compared to a sensor based on a single printed layer of the polymer.

Keywords: Inkjet printing, Carbon Nanotubes, Conducting polymers, Polyaniline, Sensors, Alcohol

1. INTRODUCTION

Carbon nanotubes have attracted much attention since their discovery in 1991, and are investigated in a vast number of diverse fields. A single wall carbon nanotube (SWNT) can be envisaged as a single graphene sheet, rolled up to form a seamless cylinder and capped at both ends by half a fullerene. In addition to this, double walled carbon nanotubes (DWNT) and multi walled carbon nanotubes (MWNT) can also be produced, where nanotubes are housed within progressively larger tubes, with a popular analogy being that of Russian Dolls. Generally, carbon nanotubes are synthesised by the breakdown of a carbonaceous source followed by recombination of short carbon dimers and trimers into tubular structures. Breakdown of the source (often methane) can be achieved through either lasers, high temperature (chemical vapour deposition, CVD), high pressure, (HiPco – high pressure decomposition of carbon monoxide) or electrical (Arc discharge) means. Other variables over which there is some control are the carbonaceous source, gas flow rate and type and size (if using nanoparticles) of catalyst. These factors, together with the production method, can be tuned to give good control over the type of nanotubes.

It is the unique properties of carbon nanotubes, such as their conducting or semi-conducting nature, that make them of interest for use in a range of applications, from composite materials to field-effect transistors.¹ They are, however, difficult to process from their as-produced state due to strong attractive interactions with each other, and their hydrophobic nature.² This so-called processing issue has to be addressed for their incorporating into materials with multifunctional or intelligent characteristics.²

Several processing methods exist, including controlled chemical vapour deposition and solution based processing.² Solution based approaches can be adapted easily for different nanotubes, dispersants and solvents, and there are an increasingly wide variety of methods for processing the resulting dispersions. These might include drop deposition, filtration, fibre spinning, spraying or inkjet printing,²⁻⁶ depending on the intended application or area of study.

Inkjet printing is an attractive processing method, as it is an “easy” relatively straightforward fabrication process, after all most of us use these printers on a daily basis for documents, and photos. These printers operate by “drop-on-demand”, ejecting small volume (10^{-12} L) droplets of ink from nozzles to create patterns. Hence it is a useful method for deposition of tiny quantities of functional “inks”, where the patterns can be designed to perform either electrical, chemical, optical or mechanical function.

In this paper we demonstrate that inkjet printing is a viable tool for processing polymer carbon nanotube composite materials.

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2. EXPERIMENTAL DETAILS

Water soluble polyaniline PMAS was synthesised following the method described by Shimizu and co-workers. 2-methoxyaniline-5-sulfonic acid (0.2 moles) was dissolved in 2.5 mL 2.5 M aqueous pyridine with stirring. This formed a yellow/green solution, and was maintained at 4°C in an ice/water bath. To the monomer, 4.5 mL APS (0.5 moles) was added drop wise over 20 minutes. With the addition of the oxidant came an increase in viscosity and colour change to dark brown. The reaction was left to proceed over 17 hours, at which point it was removed from the water bath and the stirrer stopped. The polymer was filtered through a filter paper (15 – 20 µm pore size) and washed with 100 mL methanol. A brown precipitate was collected, and dried in a vacuum dessicator overnight before being ground into a fine powder.

HiPco SWNT and CVD produced thick MWNT were obtained from Carbon Nanotechnologies Inc. (U.S.A.) and Nanocyl S.A. (Belgium), respectively.

PMAS solutions for nanotube incorporation studies were prepared by the addition of up to 100 mg PMAS to 10 mL Milli-Q water. To this, 10 mg carbon nanotubes were added and sonicated for 3 minutes at 20 % amplitude (20 W) with pulses of 2 s on/1 s off. This was repeated up to eight times, giving a total sonication time of 24 minutes. The samples were sonicated in glass vials with dimensions of 75 mm depth, 25 mm diameter, using a tip of 6 mm diameter. For UV-vis analysis, PMAS-nanotube dispersions were diluted to 0.1 mg/mL in Milli-Q water. UV-vis spectra were collected with a Perkin-Elmer Unicam UV3 UV-vis spectrophotometer between 200 and 900 nm.

PMAS and PMAS-nanotube dispersions for printing were filtered under vacuum through glass wool, before passing through a 5 µm pore size Millex-LS PTFE filter (Millipore Corporation, Bedford, MA). These “inks” were loaded into cleaned HP 51629A (black) ink cartridges through a syringe, and allowed to equilibrate for several minutes before printing with an HP deskjet 690C inkjet printer. Patterns designed in Microsoft Powerpoint were printed onto flexible transparent sheets (Impega).

Film thickness was determined from topographical analysis of the films using a white light interferometer (Veeco, Wyko NT 1100). Transmission spectra of printed films were recorded with the aforementioned UV-vis spectrophotometer. Raman spectra were collected on the films and HiPco SWNT powder with a Jobin Yvon Horiba high-resolution LabRam inverted spectroscopic microscope spectrometer, with 632.8 nm excitation line. Optical microscopy images were obtained using an Olympus BX51 optical microscope fitted with a DP50 digital camera.

Current-voltage measurements were carried out using an Agilent 33220A Waveform generator coupled to a Thurlby Thandar Instruments digital 1906 multimeter (films were contacted with copper contacts). Sheet resistance and conductivity were determined using a JANDEL four-point probe resistivity system (model RM2).

Sensing studies were carried out by an in-house design comprising a nitrogen-gas cylinder, an evaporation chamber, a measurement chamber, and flow meter connected in series. Nitrogen gas was used as the carrier gas to flow ethanol vapor from the evaporation chamber to the measurement chamber. The electrical current at constant voltage across the films was monitored with the digital multimeter.

3. RESULTS AND DISCUSSION

The interactions between PMAS and carbon nanotubes are of interest, as they might give an indication as to which type of nanotubes will be best suited to inkjet printing of composite materials. Nanotubes differ, largely due to their production method, in size (number of walls, length and diameter), orientation (straight or bent/curved, caused by five or seven membered rings) and graphitization (amount of sp² hybridized carbon relative to sp³ hybridized). At present it is not entirely clear which of these parameters affect nanotube interactions with a dispersant, so here two different types of nanotubes were mixed with PMAS through sonicating. Dispersions were sonicated for a total of 24 minutes, and after 6, 12, 18 and 24 minutes, an aliquot was removed for UV-vis analysis. Figure 1 shows the UV-vis spectra of PMAS solution, PMAS-SWNT dispersion and PMAS-MWNT dispersion at these sonication times.

The reason for removing samples during the mixing procedure was to determine how much sonication is required for nanotube stabilisation in solution. In other studies⁶ we have shown that the molecular weight of PMAS decreases from around 8650 Da to 7100 Da when sonicated for 1 hour, which represents significant degradation to the polymer. As the

chain length and therefore the amount of conjugation are shortened, the conductivity of the polymer may fall, and so mixing should ideally be kept to a minimum.

The PMAS spectra (Figure 1) exhibit characteristic absorptions features at 280 – 400 nm indicative of $\pi - \pi^*$ band transitions, and at 474 nm indicative of the low wavelength polaron band. Interactions between PMAS and carbon nanotubes result in the following changes: the $\pi - \pi^*$ band shifts to lower wavelength, the peak at 474 nm decreases in intensity and the absorbance from 500 nm onwards rises. These changes are in excellent agreement with our previous work^{7,8}.

Fig. 1. UV-vis spectra of PMAS and nanotube composite “inks”. (A) PMAS (blue line) and PMAS-SWNT dispersions sonicated 6 minutes (red line), 12 minutes (green line), 18 minutes (pink line) and 24 minutes (black line). Inset is an

enlargement of the features related to the van Hove singularities observed between 500 and 900 nm. (B) PMAS (blue line) and PMAS-MWNT (thick CVD, Nanocyl) dispersions sonicated 6 minutes (red line), 12 minutes (green line), 18 minutes (pink line) and 24 minutes (black line). Arrows indicate direction of shift with increasing sonication time.

The shift in the $\pi - \pi^*$ transition and decrease in intensity of the low wavelength polaron band are attributed to changes in the polymer conformation due to interactions with nanotubes, while the absorbance rise after 500 nm is believed to be directly related to the absorbance of nanotubes. It is clear that for SWNT, this absorbance rises gradually with sonication time, while for MWNT it reaches a maximum after 6 minutes. This suggests that with PMAS as a dispersant CVD MWNT are easier to disperse compared to HiPco SWNT.

When printing was attempted with as-prepared inks, clogging of the cartridge occurred frequently resulting in no deposition of ink on the substrates. Therefore filtering is an essential step for using standard HP cartridges. The UV-vis of the filtered solution and dispersions is shown in Figure 2. The increase in absorbance at wavelength above 500 nm observed for the composite dispersions indicates the presence of nanotubes in the inks. As expected this absorbance from 500 nm onwards is higher for the MWNT ink compared to that of the SWNT ink.

Fig. 2. UV-vis spectra (normalized) of filtered “inks”: PMAS (blue line), PMAS-SWNT (green line) and PMAS-MWNT (red line). Inset is an enlargement of the region from 500 to 900 nm.

Single layers of the inks were then used to inkjet printed onto transparent sheets, with patterns of simple filled rectangular boxes drawn in Powerpoint. Transmittance spectra of the printed films are shown below in Figure 3. The $\pi - \pi^*$ band between 280 – 400 nm is lost due to absorbance of the substrate, while the low wavelength polaron peak at 474 nm remains clearly visible. Printed film using nanotube inks display a decrease in transmittance at wavelengths above 500 nm, which is consistent with the absorbance behavior of the nanotubes. The optical transparency for $\lambda > 550$ nm of single printed PMAS, PMAS-SWNT and PMAS-MWNT layers is 100 %, 86 %, and 81 %, respectively.

The Raman spectrum of SWNT is well documented, and consists of three features, the radial breathing modes (RBM, below 300 cm^{-1}), so-called D-band (around 1300 cm^{-1}), and the so-called G-band (around 1600 cm^{-1}).⁹ The spectra features of the printed PMAS-SWNT were found to be identical to those of the SWNT starting material (see Figure 3).

Fig. 3. Transmittance and Raman spectra of printed films. (A) Transmittance of PMAS (blue line), PMAS-SWNT (green line) and PMAS-MWNT printed films. (B) Raman spectra (at 633 nm) of HiPco SWNT starting material and PMAS-SWNT printed film. Insets: photographs of (1) inkjet printed feature, and (2) HiPco SWNT starting material.

The optical microscopy image in Figure 4 shows that in the direction that the print head moves across the substrate, the film is quite continuous. However, perpendicular to this direction (the direction of the substrate movement through the printer) the film is not so continuous and gaps between adjacent parallel lines of film can clearly be seen. This is most likely due to poor wetting of the substrate by the ink, and could potentially be improved by altering the surface tension or viscosity of the sample, changing the substrate hydrophobicity or rotating the sample in between prints.

The current-voltage characteristics were determined under ambient conditions. The printed films exhibited linear behavior indicating that they obey Ohm's Law (Figure 4). The calculated resistances of the printed PMAS, PMAS-SWNT and PMAS-MWNT films (in air) are 30 M Ω , 125 k Ω , and 55 k Ω , respectively. The lower resistance (up to three orders of magnitude) observed for the composite films, is a well known effect whereby the presence of a conducting network of carbon nanotubes lowers the resistance of a material.

The resistance in the direction parallel to the print head movement is one order of magnitude lower than that parallel to the direction of printing. This is not surprising given the poor continuity of the film parallel to the print direction (see Figure 4). The room temperature four-point probe conductivity measurement of a single printed layer of PMAS-SWNT yielded a DC conductivity of 0.93 S/cm, and a sheet resistance of 100 k $\Omega/\square$.

Fig. 4. (A) Optical microscopy image of a printed PMAS-SWNT film, with the arrows indicating the directions parallel and perpendicular to the movement of the printhead moved over the substrate. (B) Current-voltage characteristics of printed PMAS (blue line), PMAS-SWNT and PMAS-MWNT parallel to the print direction.

The sensitivity of the printed films to alcohol vapours was examined, as it has been found that sensors with carbon nanotubes can show good sensitivity to a range of analytes.¹⁰ In our sensing measurements, the current of the printed films at a fixed voltage was measured over time while ethanol was periodically introduced to the chamber. A typical profile for PMAS and PMAS-SWNT printed films is shown in Figure 5. The observed fall in current with exposure to ethanol vapour corresponds to a rise in the resistance of the film. This might be attributed to swelling of the polymer increasing the distance between adjacent nanotubes, or charge transfer between the polymer and the nanotubes, both of which are known to occur from studies by other groups.

The PMAS film, due to its high resistance, gave a negligible change in current which was largely indistinguishable from the baseline noise. Therefore a single printed PMAS layer does not function as an alcohol sensor under these conditions, unless significantly higher operating voltage is used.

The more conducting PMAS-SWNT films gave a measurable decrease in current shortly after ethanol exposure, with the current slowly returning to its original value. The change in current corresponds to a decrease in resistance of 14 %. Similar results were obtained for PMAS-MWNT films. Thus, an alcohol sensor based on a single printed PMAS-nanotube layer can operate at a lower voltage compared to that of a sensor based on a single printed PMAS layer. The sensitivity towards other alcohols and limit of detection of these sensors have been reported in reference 5.

Fig. 5. Response (current at 5 V) of PMAS and PMAS-SWNT films (single printed layer) to ethanol over time at nitrogen gas flow rate of 1 mL/s. The dashed line indicates the introduction of ethanol.

4. CONCLUSIONS

In summary, it has been shown that inkjet printing is a viable tool for processing polymer carbon nanotube composite materials. The interactions between water-soluble polymer PMAS and two different types of carbon nanotubes were utilized to fabricate water soluble carbon nanotube containing “inks”. These “inks” were inkjet printed onto transparent sheets, yielding conducting transparent films. Patterns having a conductivity of 0.93 S/cm and optical transparency of 85% were obtained from a single printed layer of SWNT containing ink. An alcohol sensor based on a single printed

PMAS-nanotube layer could operate at a lower voltage compared to that of a sensor based on a single printed PMAS layer. This work contributes to the development of inkjet printing of polymer carbon nanotube composite films.

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