Inkjet Printing of Single Walled Carbon Nanotubes

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A single-wall carbon nanotube (SWNT) transparent conductive film (TCF) was fabricated using a simple inkjet printing method. The TCF could be selectively patterned by controlling the dot size to diameters as small as 34 μm. In this repeatable and scalable process, we achieved 71% film transmittance and a resistance of 900 ohm/sq sheet with an excellent uniformity, about ± 5% deviation overall. Inkjet printing of SWNT is substrate friendly and the TCF is printed on a flexible substrate. This method of fabrication using direct printing permits mass production of TCF in a large area process, reducing processing steps and yielding low-cost TCF fabrications on a designated area using simple printing.

1. Introduction

Single-walled carbon nanotubes (SWCNTs)[1] are an attractive nanoscale material for various applications, such as electronic devices, cold cathode sources, functional composites, energy storage devices, sensors, and actuators.[2-7] Extensive research has been conducted on transparent conductive films (TCFs) based on SWCNTs because the display industry requires a substitute for indium tin oxide (ITO), the quantities of which are limited and therefore increasingly expensive.[8] Flexible SWCNT TCF is particularly desirable for application in flexible displays in the near future. For these reasons, researchers have become increasingly interested in SWCNT-assisted TCF, which may satisfy the requirements of high conductivity and excellent flexibility at a much lower cost than ITO. Previous methods of fabricating SWCNT TCF have included roll-to-roll printing based on polymer composite, vacuum filtering, line patterning, dip coating, screen printing, and spray coating.[9-14] Ideally, TCF performance and productivity should be based on a simple, reliable fabrication method that is cost efficient and requires few steps.

Inkjet printing is a popular method used in the conventional printing industry due to fine and arbitrary pattern generation, non-contact injection, solution saving effects, repeatability, and scalability, all of which are advantageous to large area processes.[15-16] Inkjet printing of SWCNTs can readily control film thickness, homogeneity, and uniformity. It also enhances the scalability of the patterning and reproducibility. Although recent studies have reported inkjet printed multi-walled carbon nanotubes (MWCNTs), this film has lower transparency and has greater resistance than conventional TCFs.[17] To date, no studies have reported SWNT-based inkjet printing for TCF.

This paper introduces a simple and process-efficient inkjet-printed SWCNT TCF that has a low sheet resistance at a given transparency.

2. Fabrication

In our experiment, a single inkjet head (MicroJet™, 50 μm) equipped with a piezoelectric actuation module ejected SWNT ink solution onto a glass or polymer substrate. The SWCNTs (Iljin Nanotech, Korea) were synthesized using arc discharge, purified with acid, and then filtered centrifugally, as in the nominal purification process.[18] The diameter and length were 1~1.2 nm and 5~20 μm, respectively. The purified CNT powders were dispersed in dimethylformamide (DMF) at a density of approximately 10 μg/ml, and then sonicated for 2 h to disperse them uniformly.[19]

During the printing process, the jetting conditions were tuned to generate uniform ink drops; these were affected by the viscosity and surface tension of the ink, jetting speed, particle size, substrate surface condition, humidity, and environmental temperature.

Thermal treating was also performed to improve the film quality since the SWNT solution drying time is critical to the fabrication of uniform SWNT networks. On bare glass, the ink solution usually dried in 12 s at room temperature. Heating at 60°C produced a significant reduction in time to less than 1.6 s.

Use of hydrophilic plasma-treated glass contributed to a reduced drying time as well as an overall uniform evaporation of the dropped solution. When the solution dried slowly at room temperature, it produced a 'coffee ring' effect with SWNTs densely deposited in the center, as shown in Fig. 1(c). This phenomenon was caused by faster drying at the periphery of the solution drop, and repeated drying caused an uneven density distribution.[20] Therefore, a slow drying process caused two different dense regions at the middle and the periphery. In contrast, a short solution drying time resulted in a uniform SWNT network because, for the most part, the dropped solution evaporated instantly as it was exposed to air (see Fig. 1(d)).
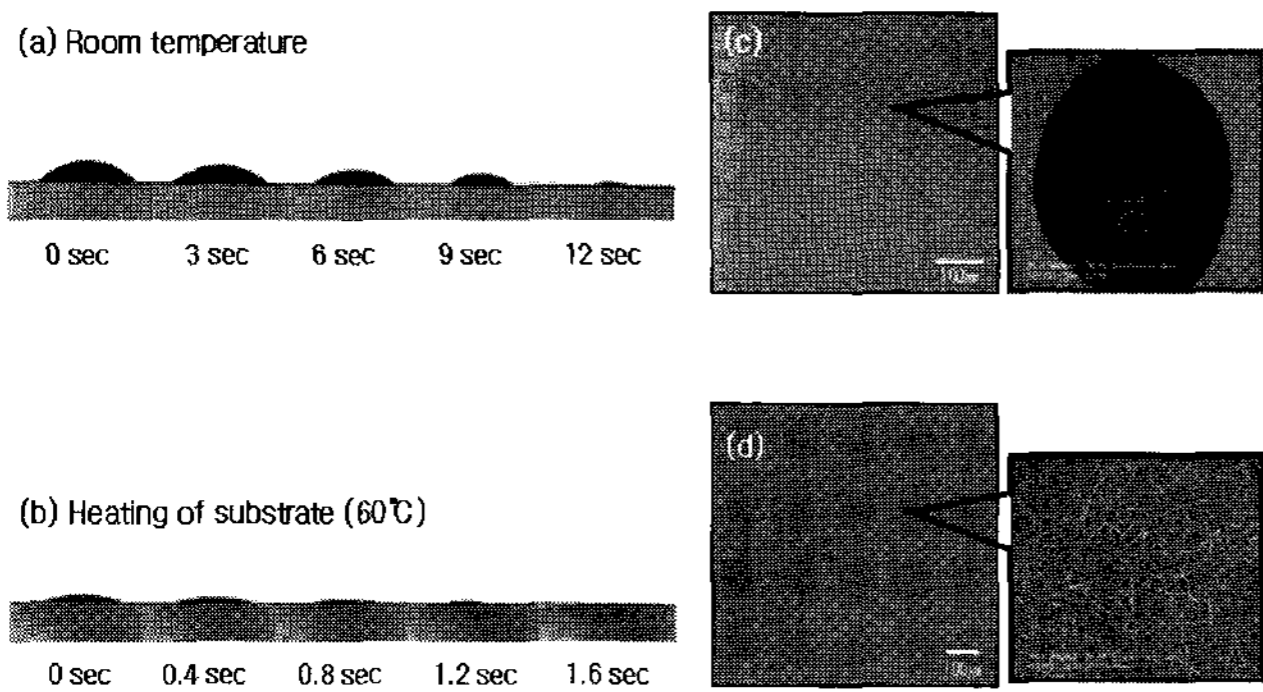
Fig. 1 Drying behavior of dropped solution and the formation of the SWNT network after drying: (a) drying process on bare glass at room temperature and (b) drying process on bare glass at 60°C. (c) A 'coffee ring' effect formed under slow drying conditions. (d) Uniformly dried solution with heating. Insets show enlarged images of the indicated area, revealing (c) non-uniform dense flocculation and (d) uniformly networked SWNT.

3. Discussions

Features of inkjet-printed SWNT TCFs were characterized in terms of transmittance, sheet resistance, and uniformity. The film sheet resistance was inversely proportional to its transparency according to the time of printing, as shown in Fig. 2. Measurements using a UV-vis spectrometer (Shimadzu, UV-3600) revealed that the ultraviolet (UV) wavelength range appeared to have a lower optical transmittance than the visible range. A higher transmittance in the visible wavelength region explains the effect of partial interception by UV rays.

The sheet resistance was measured with a four-point probe (AIT, CMP-100MP) at 20 different film positions. When we dropped ink from the head, no single drop was in contact with another during the first printing. If a droplet touched a previously deposited droplet, the solution merged, resulting in several SWNT aggregations after evaporation. A printing speed slower than 1.6 s could prevent this phenomenon, but this strategy would require tricky jetting conditions and slow film fabrication. Alternatively, we left a space around each droplet during the first printing and we deposited new droplets in the
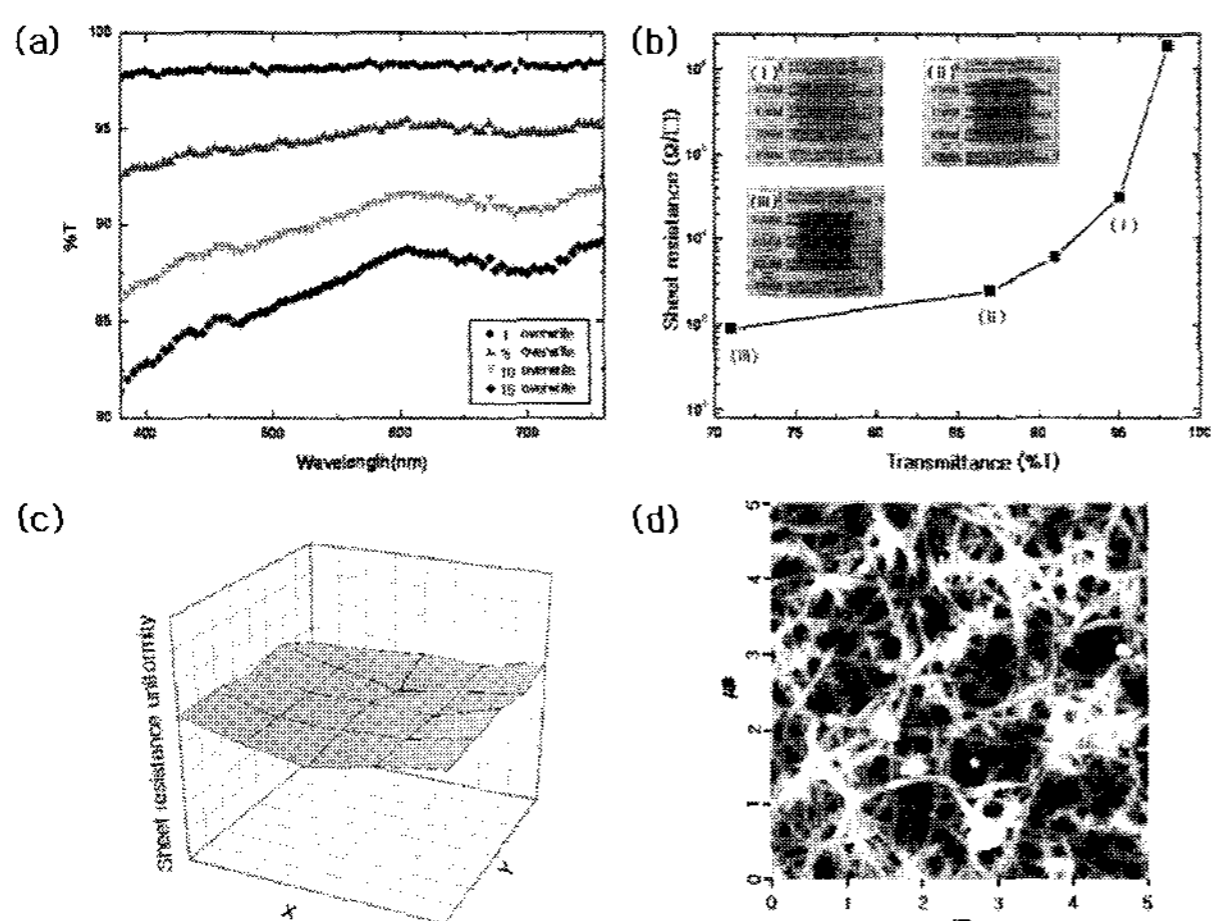
empty space during the second printing. The two printings accomplished a single overwriting process. In particular, the film with 30 overwrites had a sheet resistance of 900 (ohm/sq) and a transmittance of 71% at 550 nm (case (c) in Fig. 2(b)). This was likely a result of the non-uniform network formation caused by printing, the conductance degradation of purified SWNT samples, and weak physical contact between nanotubes in the film. The deviation in sheet resistance ranged from ± 4.4 – 5.6 %, indicating an acceptable level of uniformity similar to that for ITO film on glass. This plays an important role in practical applications of TCFs, such as their use in touch screens. An atomic force microscope (AFM) was used to measure the surface of the fabricated film (case 1 in Fig. 2(b)), which had a thickness of about 50 nm.

Inkjet printing is able to produce a pattern directly, while other methods require extra processing steps such as pattern generation and relocation. The method of directly printing TCF on an area has distinct advantages over conventional methods: it both simplifies the fabrication process and lowers the cost of industrial level TCF production. It also has great potential for TCF mass production by providing control of where it is placed. We printed SWNT solution into a pattern (the word "Nanotechnology") using different overwriting times on 5 x 5 cm^2 glass, as shown in Fig. 3(a). We were

Fig. 2 (a) Optical transmittances of inkjet-printed TCF films at 550 nm, shown as 98, 95, 91, and 87 % transmittances for 1, 5 10, and 15 overwrites, respectively. (b) Sheet resistance variation to different transmittance values: the sheet resistance linearly decreased in the range of 80 – 95 % transmittance. The inset figures show fabricated films. (c) Uniform values of sheet resistance distribution on a film. (d) AFM image of a film with a 50-nm thickness and 71% transparency.
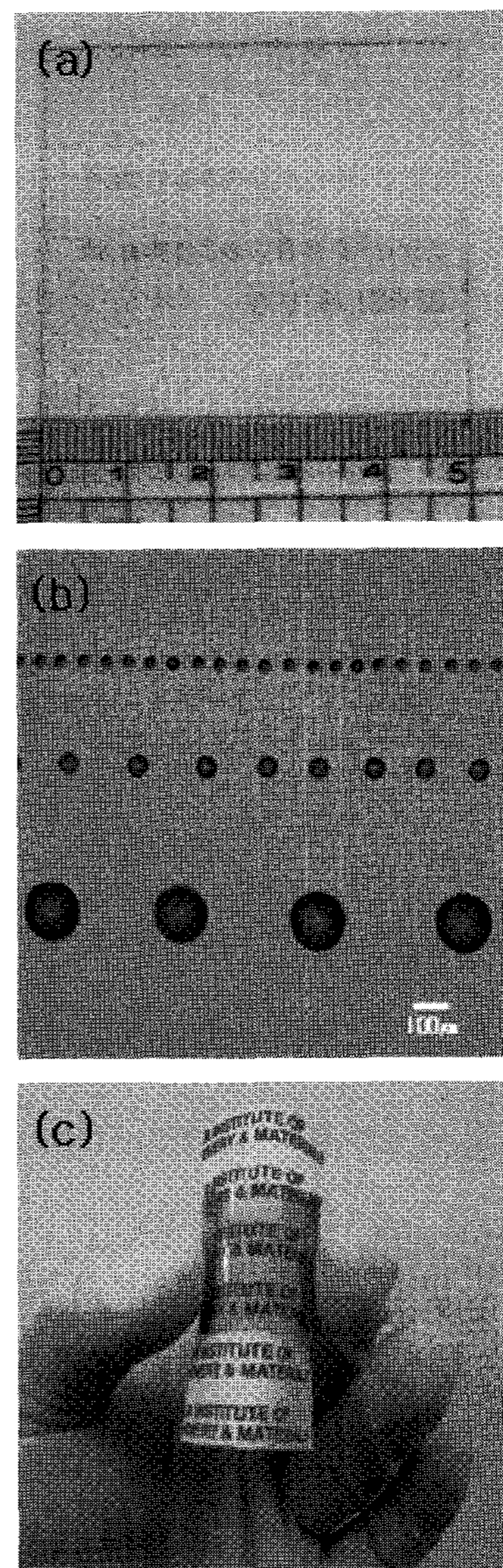

Fig. 3 Patterned printing of the SWNT solution: (a) the word "nanotechnology" was written in different transparencies using 5, 15, and 30 overwrites starting from the top of the glass. (b) Dotted line patterns made using different droplet sizes, with diameters of 34, 72, and 169 μm. (c) Transparent SWNT film printed on a PET substrate showing the film flexibility.

able to control both the transparency and image resolution of the word. The pattern resolution mainly depended on the inkjet head diameter and jetting conditions. We achieved a minimum dot size as small as 34 μm. Larger dots formed by piling up the jetting drops were as large as 72 and 169 μm, as shown in Fig. 3 (b). The dot size could also be modulated using different nozzle sizes. In addition, we directly fabricated transparent SWNT film (Fig. 3(c)) on a PET substrate and produced values of the transmittance and sheet resistance almost identical to glass substrate, indicating that various substrates can produce homogenous results. The film with 30 overwrites had a sheet resistance of 1100 (ohm/sq) and a transmittance of 76% at 550 nm. This SWNT-aided TCF fabrication on a flexible polymer substrate may broaden its applications.

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