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Optimisation of carbon nanotube ink for large-area transparent conducting films fabricated by controllable rod-coating method

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ABSTRACT

Single-walled carbon nanotubes (SWCNTs) were dispersed in water with the help of surfactants to achieve high concentration SWCNT ink. SWCNT transparent conducting films (TCFs) were fabricated by rod coating using the SWCNT ink. A combination of two surfactants provided optimal rheological behaviour, which produced uniform films by preventing dewetting and rupture of SWCNTs during drying. The combination led to a dramatic increase of shear viscosities but no change of their wettability. The viscosity of SWCNT ink was controlled by the ratio of two surfactants. The thickness of SWCNT films could be easily varied by controlling both the concentration of SWCNT ink and the size of the wire-wound rod. The produced uniform SWCNT-TCFs treated by nitric acid have a relatively low sheet resistance of ~80 $\Omega\ sq^{-1}$ at 80% transmittance. The performance has a wide range of applied interest for touch screen and flexible electronics.

1. Introduction

Since carbon nanotubes (CNTs) were discovered [1], many avenues have been explored to engineer CNTs for commercial applications due to their outstanding mechanical, optical and electrical properties [2,3]. Transparent conducting films (TCFs) based on single-walled CNTs (SWCNTs) are widely utilised in numerous applications such as thin-film transistors [4], electron field emitters [5], supercapacitors [6], organic light emitting diodes (OLEDs) [7,8] and organic photovoltaics [9]. Indium tin oxide (ITO), the conventional conductive metal oxide thin film, has been widely used as transparent electrodes. However, ITO is an inadequate solution for the next-generation devices because of the rising price and limited supply of Indium, the brittle nature and poor flexibility of ITO layer, and the high-temperature and low-pressure manufacturing process of ITO films. Therefore, the flexible and low-cost CNT films will be a prospective alternative to replace ITO films [10–12].

CNT-based TCFs (CNT–TCFs) have been fabricated by direct growth and solution-based deposition methods. Solution-based deposition consists of vacuum filtration [13], spin coating [14], spray coating [15,16], dip coating [17], inkjet printing [18], gel coating [19], Mayer rod coating [20] and self-assembly methods [21]. Each method mentioned above has its own characteristics. In particular, Mayer rod coating is one of the most popular coating methods. The Mayer rod is a stainless steel rod that is wound tightly with stainless steel wire of varying diameter. The wet thickness of CNT films after coating is directly proportional to the diameter of the wire used. The amount of liquid remaining in the coating is governed by the cross-sectional area of the grooves between the wire coils. If this liquid spreads uniformly, one would expect the coating thickness to be 10.7% of the wire diameter. In

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the coating process, other physical factors may influence the actual coating thickness. Therefore, the transmittance of CNT films is varied by controlling both the concentration of CNT dispersion and the diameter of the wire used [22]. The sheet resistance and transmittance of CNT films rely on the coating thickness and both decrease with the increase of film thickness [23]. We will discuss the relationship between transmittance and sheet resistance of films in this article.

Mayer rod coating can easily generate large-area films on suitable substrates. No CNT ink is wasted and no high temperature is needed during the process. This will significantly reduce the costs. Mayer rod coating has stringent requirements for the dispersion rheological behaviour. Coalescence, wetting, levelling, dewetting and crawling are the processes that are strongly influenced by surface tension and viscosity of the solution. Surface tension plays a very important role in wettability; a number of defects can be caused by surface forces. For a liquid to wet a surface, its surface tension has to be lower than the surface energy of the solid. In order to achieve this goal, surfactants are used to lower the surface tension of the solution, and the surface energy of the substrate can be increased by oxygenating the surface. For example, recent reports have indicated that fluorosurfactants are effective in lowering surface tension for uniform coating [24]. Good wettability can be also acquired by increasing the surface energy of the substrate using corona discharge treatment. Levelling is the critical step to get a smooth and uniform coating. The surface levelling process is driven by surface tension and resisted by viscosity [25]. The shear viscosity is defined as the ratio of the shear to the shear strain rate [26]. To facilitate levelling, therefore, it is desirable to employ coating with low viscosity. Nevertheless, it is difficult to deposit heavy coating and hinder the secondary flow caused by dewetting if the viscosity is low [27]. The key to obtain an optimal coating is the balance between surface tension and viscosity.

In this article, we report the fabrication of SWCNT films by “Mayer rod coating” at room temperature. A combination of two surfactants provided optimal rheological behaviour for the process, which produced uniform films by preventing the dewetting and rupture of CNTs during drying. We also compared the performance of TCFs using SWCNTs of different purity.

2. Experimental

2.1. Preparation of SWCNT ink

SWCNTs with different purity (90 and 95 wt%, purity of carbon:carbon + metal) synthesised by chemical vapour deposition (CVD) method were purchased from Chengdu Organic Chemicals Co., Ltd. High purified SWCNTs (purity 97 wt%) synthesised by an arc discharge method were purchased from Hanwha Nanotech. The SWCNT powder (0.1 wt%) was added into a 30-ml aqueous solution dissolved with sodium dodecylsulphonate (SDBS) (1 wt%) or hexadecyl trimethylammonium bromide (CTAB) (1 wt%) as surfactant. The solutions were dispersed by a horn-type sonicator at 40 W for 60 min and followed by centrifugation at 5000 rpm for 30 min. The supernatant of the SWCNT–SDBS dispersion was collected from each centrifuge tube using a pipette. The above procedure typically produces a uniform SWCNT–SDBS suspension. The concentrations were similar to the initial concentrations before centrifugation because of the high dispersion. Then Triton X-100 (TX100, ranged in 0.5–3 wt%) was added into SWCNT–SDBS dispersion, stirring at 50 °C for 10 min in water bath.

2.2. Fabrication of TCFs

The TCFs with varying transmittance were fabricated using the Mayer rod equipped with wires of diameters from 0.05 to 1 mm (R. D. Specialties), and then the coated films dried either at room temperature or on a hot plate. The dried TCFs were immersed in deionised water for 30 min to remove a majority of surfactants and followed by drying at 80 °C for 30 min to avoid the CNTs detaching from the polyethylene terephthalate (PET) films. Then, the TCFs were rinsed in deionised water for several times to further remove the surfactants. Finally, TCFs were immersed in 12 M nitric acid for 40 min followed by washing with deionised water and dried again [15].

2.3. Characterisation

Contact angle characterisation was carried out by a contact-angle analysis device (DSA100, KRUSS). Shear viscosity was performed by rheometer and surface tension was characterised by automatic surface tensiometer (BYZ-1) at room temperature. UV–vis spectrometer (UV-1901) was employed to analyse the film transmittance and the sheet resistance was measured with a four point probe (Keithley-2700). The morphology of the films was observed using scanning electron microscope (SEM) (HITACHI S-4800); some CNTs could be scraped off from PET substrate and transferred to copper grid for transmission electron microscope (TEM) (TECNAI-20), while Raman spectra were gained via a Raman spectrometer (RENISHAW) with a laser excitation wavelength of 532 and 633 nm.

3. Results and discussion

The coating facility in our work consists of a glass drawdown pad and a stainless steel rod wrapped tightly with stainless steel wire, similar with the schematic illustrated by Dan et al. [27]. The substrate is held down on the glass pad using a clamp; coating liquid is applied to the substrate ahead of the coating rod with a dropper, excess coating liquid can be doctored off in rod coating. The amount of liquid remaining in the coating is related to the gap between the high points of the wires. The geometry of this system creates a wet film thickness directly proportional to the diameter of the wire used. The initial shape of the coating is a series of stripes spacing apart according to the space of the wire windings. The thin film also can be regarded as an ideal sinusoidal surface [25]. Owing to surface tension, there will be a pressure differential across liquid and air interface. This pressure difference promotes flow from peaks to valleys and forming a