

# CARBON NANOTUBE COMPOSITE FILMS WITH SWITCHABLE TRANSPARENCY

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## Introduction

Optical switchable windows (OSWs) have attracted great interest in the areas of privacy and solar control. Their practical applications range from electrical shutters, smart auto windows to projection screen and band-pass filters [1]. In the conventional fabrication of OSWs, the coating of chromic materials on transparent indium tin oxide (ITO) allows the control of incident light transmission when an electric, thermal, or chemical stimulus is applied [2]. However, due to the sharp shortage of indium resources on earth and increasing demands for flexible transparent devices, it's imperative to develop new materials and technologies to replace ITO and prepare OSWs with multi-functions.

More recently, tremendous attention has been paid to developing carbon nanotube (CNT) thin films as a promising ITO alternatives for functional devices and composites, for instance, transparent and flexible conductors, loudspeakers, heaters, incandescent displays, etc [3]. Here, we report a CNT-polyurethane (PU) composite film with switchable transparency. By modifying the structures of PU, the composite film show switchable transparency with good reversibility under a low voltage. Such smart composite film can be easily produced in large scale, switching transparency with chosen color backgrounds, and being coupled with optoelectronic devices. This work may pave an easy path to novel flexible OSWs at low cost.

## Experimental

### Materials

Polyurethane (PU) was obtained from Changzhou Sanhekou Polyurethane Factory, and used without any post-treatment.

Carbon nanotube films were drawn continuously out of a super-aligned CNT array grown by chemical vapor deposition method (CVD) in our own laboratory. The CNT arrays used here were about 200 $\mu$ m tall with good spinnability. And there are two kind of CNT arrays: is few-walled (FWCNT, diameter  $\sim$ 6 nm, 2-3-walled) and multiwalled (MWCNT, diameter 8-10 nm,  $\sim$ 6-walled).

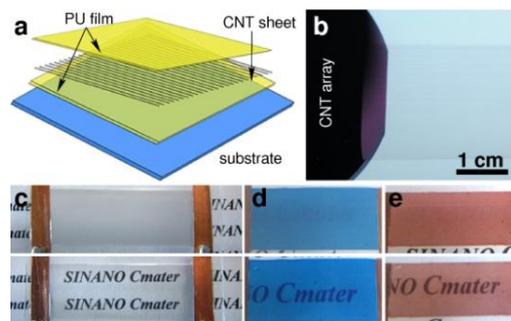
The sandwich structure of the CNT/PU composite film is shown in Figure 1a. The PU sheets were prepared on a glass substrate by evaporating the solvent of the PU solution in N,N-dimethylformamide, with a concentration of 10–20 wt%. Then lay the CNT film between two layers of PU sheets, and electrodes were fabricated directly on two ends of CNT film to ensure good contact.

### Apparatus and Procedures

The DSC measurement was performed over a temperature range of 25–200  $^{\circ}$ C using a Seiko DSC-6220 thermal analysis system, with a heating rate of 2  $^{\circ}$ C/min. Polarized Optical Micrograph (POM) was performed on a Leica DM4000M with crossed polarizers to trace the phase transition procedures of the polyurethane. The transmittance of the composite film was determined with an Analytik Jena's SPECORD S600 spectrometer. Optris CT LT infrared thermometer was used to characterize the temperature variation of ohmic heating.

## Results and Discussion

The composite film, initially opaque (Figure 1c, top), became transparent in just a few seconds when a certain voltage was applied (Figure 1c, bottom). It turned back slowly to the opaque state when the voltage was turned off. The reversible change between opaque and transparent can be also observed in two dyed CNT/PU films, see images d and e in Figure 1. Without the introduction of CNTs, the opaque-to-transparent transition is simply a thermal effect of the PU soft segments which undergo a crystal melting at 52  $^{\circ}$ C, as indicated by the endothermic DSC peak for a PU film (Figure 2a). Before the melting, the soft segments crystallized in randomly distributed large-size spherulites, see the POM image in Figure 2b. After the transition (not shown here), the spherulitic parts turn to amorphous due to the disassembly and entanglement of the PU molecules.



**Figure 1.** (a) Layered structure of a CNT/PU composite film. (b) A transparent and uniform CNT sheet is drawn from an array. (c, d, e) The opaque (top) and transparent (bottom) composite films induced by electric current.

After CNTs are introduced, the PU film becomes electrically conductive, with a relatively high resistance about 1000  $\Omega/\square$ . As a result, the film can turn to

transparent because of an ohmic heating (Figure 1c-e) under an electric current. Note that the transition is not simply a thermal effect as observed in the PU film, because the crystallization kinetics and thermal behavior of the soft segments in PU have changed significantly. For example, the melting temperature has decreased from 52 °C to ~47 °C due to the existence of CNT films (figure 2a). This decrease probably arises from the changes in size and alignment of the spherulites as shown in Figure 2c-e.

CNTs also make the transparency switching more rapid than that of the pure PU, and interestingly, less sensitive to the environmental temperature. It usually takes about 20 s for a PU film to be transparent on a hot stage with a temperature of 60 °C. However, the 1.4-cm-long MWCNT/PU film can be transparent in less than 5 s when the voltage higher than 30 V, see Figure 3a. The film exhibited the same fast switching of transparency at a low temperature of 0-4 °C inside a refrigerator. This temperature insensitivity ensures the application of the film at low temperatures. The response time as a function of voltage is plotted in Figure 3b, which is defined as the time to reach the half of the full transmittance (~80% and 90% for the MWCNT/PU and FWCNT/PU films).

In figure 3c, square resistances in air of three MWCNT/PU films and a pure MWCNT sheet were plotted against the current normalized by film width. It clearly shows a decrease in resistance with increasing current. From these plots, we can see the safe working current should be no larger than 4 A/m. or else, the film temperature may do harm to real applications. A smart way to use such temperature-current relation is to activate the transparency at a high voltage (30-35 V) and maintain the transparency at a low voltage (<15 V). Considering the transparency-opaque transition should

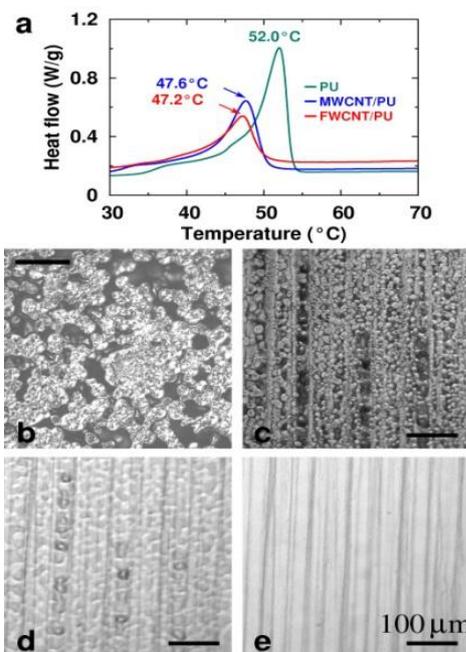


Figure 2. (a) DSC scanning of PU, MWCNT/PU, and FWCNT/PU films. (b) POM image showing the large-size spherulites (15- 40 μm) in the pure PU. (c-e) POM images of an MWCNT/PU film at 0, 5, and 15 s, after connected to a voltage of 30 V. After the voltage turn-off, the composite film can recover back to (c). Scale bars are all 100 μm.

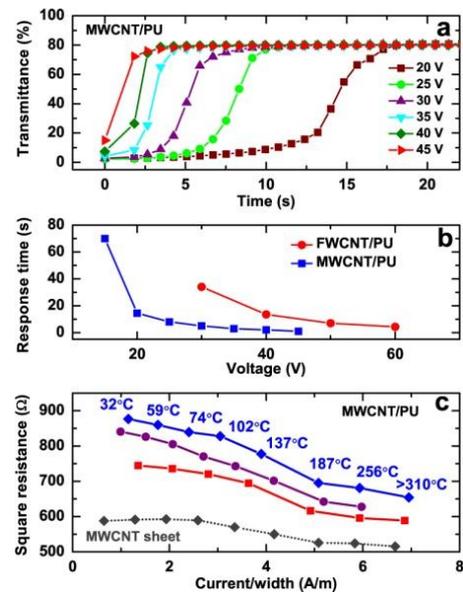


Figure 3. (a) Time evolution of 550 nm transmittance for an MWCNT/PU film connected to various voltages. (b) Response time obtained from (a) The films were 1.4 cm in length. (c) Square resistances of three MWCNT/PU films and an MWCNT sheet as functions of electric current per unit film width.

take about 10min, we found that the power consumption was only 0.01 W/cm<sup>2</sup>. The low energy consumption of the transparent composite film is due to the small thermal conductivity of PU (~0.2W/m K for the nonporous PU) [4], which is several orders of magnitude smaller than those of copper (401W/(m K)) and CNTs (~3000 W/(m K)).

## Conclusion

The CNT/PU composite film can be electrically conductive, flexible, and switchable from opaque to transparent under various environments. Very low mass fraction (<0.2 wt %) of CNT film incorporated into PU sheets, results in smaller and aligned spherulites of PU along CNT bundles, and a lower transition temperature. Because of the easy synthesis and sufficiently low power consumption to maintain the transparency, such a method can be potentially used in large-size OSWs at a very low energy cost.

## References

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