

Patternable transparent carbon nanotube films for electrochromic devices

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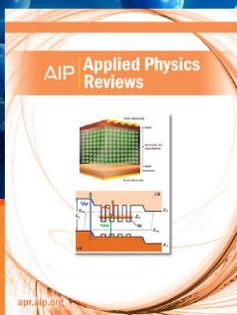
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Patternable transparent carbon nanotube films for electrochromic devices

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This paper reports the application of transparent single walled carbon nanotube films on polyethylene terephthalate as flexible electrodes in electrochromic devices using polyaniline as the active layer, where Sn-doped In_2O_3 on plastic is not suitable due to its high sensitivity to acids. Patterning of nanotube films with resolution of $50\ \mu\text{m}$ is achieved by simply using the transfer printing method based on polydimethylsiloxane stamps. The combination of high optical transparency, low sheet resistance, robust mechanical and environmental stabilities, and ease of patterning of nanotube films meets the requirements for flexible voltage-driven type of displays.

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Transparent electrodes on flexible substrates are essential supporting materials for applications such as bendable displays and plastic solar cells.^{1,2} Traditionally, Sn-doped In_2O_3 (ITO) is used; however, deposition of this transparent conductor on flexible substrates generally reduces its performance. For example, typical conductivities of ITO on polyethylene terephthalate (PET) are about five times lower than that on glass.³ In addition, cracks develop after repeated bending or strain^{4,5} and it is not resistant to acid.^{6,7} Because of these technical deficiencies, there is an increasing need for alternative materials for use as flexible transparent electrodes.

Single walled carbon nanotubes (SWCNTs) exhibit both high conductivity ($10^6\ \text{S/cm}$) and high current-carrying capacity ($10^9\ \text{A/cm}^2$).^{8,9} Films made of randomly distributed SWCNTs have also been shown to possess excellent performance with low sheet resistance and high optical transparency as well as robust mechanical flexibility and thermal stability.¹⁰⁻¹⁴ As of today, several methods such as filtration, spraying, self-assembly, and spin coating have been developed for fabricating nanotube films.¹⁰⁻¹⁴ Devices such as organic light emitting diodes,^{15,16} solar cells,^{17,18} and transparent transistors^{19,20} have been demonstrated using films with performance comparable to those for which ITO electrodes are used. Recently we have developed a simple method based on a filtration and transfer printing process.²¹ Patterned films can be printed onto a variety of substrates including silicon, glass, PET, polymethyl-methacrylate (PMMA), and many others.

Electrochromic devices attract much interest due to their potential use in applications such as smart windows, electronic paper, and wearable displays.²²⁻²⁴ For flexible electrochromic devices, the development of transparent electrodes

on plastic substrates is needed. Many electrochemically driven electrochromic devices involve the use of corrosive electrolytes, thereby precluding the use of ITO on plastic substrates. Some conducting polymers such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT/PSS) show promise to attack this problem,^{25,26} although their conductivity as well as thermal and chemical stabilities are still in need of improvement. In this Communication, we use SWCNT films on PET substrates as transparent electrodes in flexible electrochromic devices with polyaniline as the active material. We find that, in terms of the attributes required for this application including mechanical flexibility and environment stability, the performance of SWCNT films is superior to that of ITO on plastic substrates.

The color or the optical transmittance of the conducting polymer polyaniline is dependent on its oxidation state, which can be conveniently monitored by the potential applied to the polymer.²²⁻²⁴ Polyaniline will exhibit electrochromic behavior only in an acidic environment because polyaniline is dedoped in neutral or basic environment and becomes electrically insulating.²⁷ Using this polymer as the active material for electrochromic devices requires the electrodes to be resistant to the acidic erosion. This polymer has been previously used in electrochromic devices with ITO on glass as the transparent electrodes.²²⁻²⁴ Polyaniline films can be deposited onto electrodes via a simple electrochemical reaction in an acidic solution.²⁸⁻³⁰ In our work, polyaniline is electrochemically grown on thin ($\sim 30\ \text{nm}$) SWCNT films. Films with $150\ \Omega/\text{sq}$ sheet resistance and 80% transmittance at 550 nm fabricated by a printing method²¹ were used for the conducting polymer deposition. A nanotube film was dipped into $1.0\ \text{M}\ \text{H}_2\text{SO}_4$ for 2 h and no change in the sheet resistance or transparency was observed after subsequent washing and drying. For comparison, ITO on flexible PET substrates (Conducting Polymer Films Inc.) was found to dissolve in the same solution in less than 1 min.

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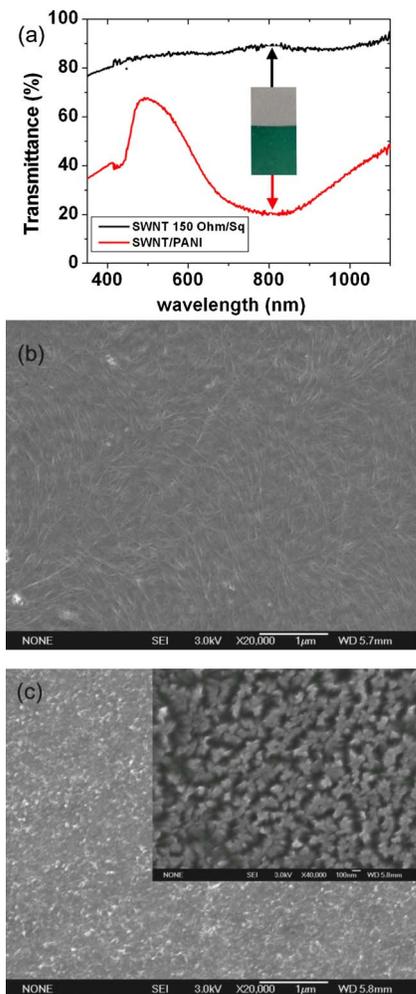


FIG. 1. (Color online) (a) Transmittance vs wavelength for a bare (upper curve) and polyaniline covered SWCNT film ($150 \Omega/\text{sq}$) after coating for 5 min at 0.8 V (lower curve). Inset is a photograph of the SWCNT film. (b) A SEM image of a thin (approximately 30 nm) SWCNT film on a PET substrate. (c) A SEM image of polyaniline coating and the insert shows the close look of the surface.

After the film was printed onto the PET substrate,²¹ the bottom half was immersed into 0.1M aniline solution in 1.0M H_2SO_4 for a 5 min electrodeposition, which was carried out on a Princeton Applied Research Potentiostat/Galvanostat (model 263A) using a saturated calomel reference electrode (SCE). The counter electrode was a Pt wire. A constant potential of 0.8 V versus SCE was applied to the SWCNT film side. The transmittance of the films with and without polyaniline coating was measured using a Beckman Coulter DU 640 spectrophotometer. The photograph in Fig. 1(a) shows the sample, the lower half of which has been submerged into the polyaniline solution. One sees that the bare nanotube film is transparent in the visible range and that the covered film has a transmittance peak near 500 nm corresponding to the green color of the polymer. Figure 1(b) displays a scanning electron microscopy (SEM) image of the nanotube film on a PET substrate. The surface roughness as determined by atomic force microscope (AFM) imaging was found to be approximately 10 nm. Figure 1(c) shows the same film coated with homogeneous polyaniline, and the inset shows a close look at the polymer surface with distrib-

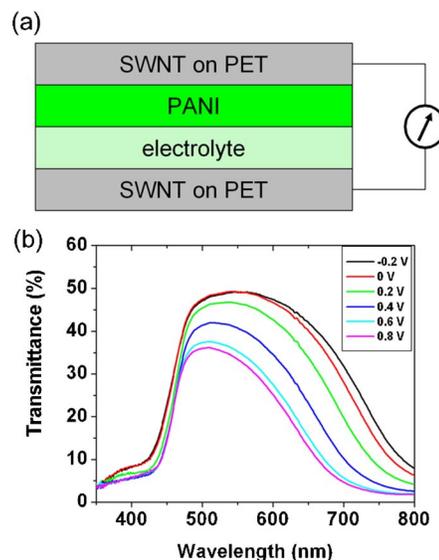


FIG. 2. (Color online) (a) A schematic representation of an electrochromic device where the electrolyte is 1.0M H_2SO_4 (b) The transmittance of electrochromic devices under various potentials ranging from 0.8 to -0.2 V.

uted island structures. The thickness of polyaniline coating is approximately 30 nm from AFM imaging.

A schematic diagram of the electrochromic device is shown in Fig. 2(a). One nanotube film ($150 \Omega/\text{sq}$ sheet resistance and 80% transmittance at 550 nm) with polyaniline coating was used as the top half cell, and an identical uncoated film was used as the opposing cell. Sandwiched between them was the electrolyte, 0.1M H_2SO_4 , with a thickness of approximately 3 mm. A voltage was applied across copper wires connected to the ends of SWCNT films. A visible color contrast upon switching the potential from 0.8 to -0.2 V is evident. The device exhibits green color at 0.8 V and yellow color at -0.2 V. Both colors are uniform over a relatively large area ($2 \times 2 \text{ cm}^2$), which indicates that the SWCNT films are homogeneous and highly conducting resulting in a uniform voltage distribution. Figure 2(b) shows the voltage dependent transmittance of the assembled device. The peak transmittance is 50% at 550 nm under -0.2 V and 35% at 500 nm under 0.8 V, which corresponds with the color change. The highest electrochromic contrast is at 625 nm with a transmittance change $\Delta T=25\%$. The contrast could be increased by using other active materials or a combination of complementary electrochromic active materials.³¹ The switching time between the two colors was measured by reversing the potential from 0.8 to -0.2 V and found to be approximately 10 s, which is comparable with that of polyaniline based electrochromic device using ITO/glass as electrodes.³²

One advantage of printed SWCNT films is that the binding between nanotube and the substrate is strong; this may be due to the heat treatment in the printing process or perhaps to the hydrophobic interactions between nanotubes and the substrate. The film formed on the PET substrate cannot be removed through cellophane tape test.²¹ Stability tests conducted on the devices further confirmed this strong binding. The device was submitted to 100 charge/discharge cycles immediately after fabrication and again one week later, and it

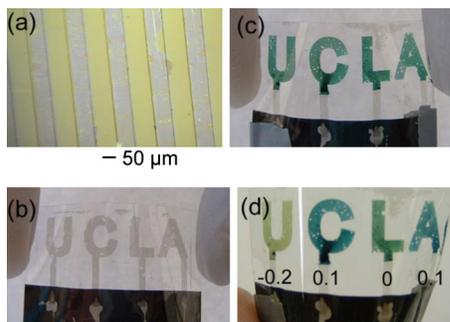


FIG. 3. (Color online) (a) Patterned nanotube film lines on PET substrates. (b) Patterned SWCNT films on PET, where the horizontal length of each letter is approximately 1 cm. (c) The films after a 5 min polyaniline deposition. (d) The photo for the top half cell taken immediately after being removed from the device, where each letter is under a different voltage. Films shown in (c) and (d) were bent to demonstrate the flexibility.

was found that the green and yellow colors changed repeatedly with no obvious degradation. For comparison, when conducting polymer PEDOT/PSS was used as a transparent electrode, it was observed to shrink and then peel off from the substrate after several minutes of exposure to water.³³

To pattern nanotube films on PET, two steps were involved: patterning the polydimethyl siloxane (PDMS) stamp using a master and transfer printing the films. To pattern the master, a silicon substrate was baked for 15 min at 150 °C, and SU-8 photoresist was spun onto the silicon wafer for 30 s at 4000 rpm, which produces a 20 μm thick resist layer. This was followed by a soft bake at 65 °C for 3 min and 90 °C for 4 min. The material was exposed to 405 nm light through optical masks for 75 s at a power of 8 mW/cm². The postexposure baking procedure was the same as the soft bake. After 5 min development using SU-8 developer, the sample was rinsed by isopropyl alcohol and blown dry. Finally, the master was treated for 2 h in the vapor of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane. To transfer the SWCNT film, we first made conformal contact between the patterned stamp and the film on the filter. As soon as the wetting due to the conformal contact was seen, the stamp was raised from the filter and the patterned film was thus transferred onto the stamp. The PDMS stamp was then contacted onto the receiving substrate. After mild heating at 80 °C for 20 min, all patterned films on the stamp were transferred onto the receiving substrate by simply removing the stamp from the substrate. Figure 3(a) is an optical image of the patterned films on PET. The gray lines are nanotube films and the distance between the lines is 50 μm which meets the size requirements for certain display applications.³²

Patterned films allow fabrication of electrochromic devices with desired configurations. SWCNT films with a size of approximately $1 \times 1 \text{ cm}^2$ on a PET substrate [Fig. 3(b)] were used for polyaniline deposition by applying voltage across the bottom lines of the “UCLA,” which resulted in uniform coating as shown in Fig. 3(c). A device was assembled using the structure in Fig. 2(a), where the patterned film replaced the top half cell. The letters display different colors [Fig. 3(d)] under different applied voltages (−0.2, 0.1,

and 0 V). The photograph shows only the top half cell of the assembled device and demonstrates that the film can be bent to a large angle without destroying the SWCNT films and the polymer coating (as determined by subsequent device measurements). The color stays unchanged for approximately 20 s after removing the SWCNT films from the device. The size of the letters in Figs. 3(a)–3(d) appears different due to the different amounts of bending. No cracks were observed under the optical microscope after bending the top half cell to a radial angle of 160° 100 times.

The performance of 80% transmittance in visible range and 150 Ω/sq sheet resistance meets the requirement of general voltage-driven (no current between the two electrodes) displays based on mechanisms such as electrowetting of liquid,³⁴ electrochromic effect of conducting polymer, electrophoretic effect of microparticle ink,³⁵ etc. Patterning of SWCNT films with 50 μm resolution has been shown, which could be improved by using other master fabrication methods to get high ratio PDMS stamps.³⁶ The mechanical flexibility, ease of patterning, and excellent chemical stability show that SWCNT films are ready to be used as robust transparent electrodes also for other applications such as photochemical cells, touch screens, and “see-through” microfluidic devices.

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