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# Organic solar cells using few-walled carbon nanotubes electrode controlled by the balance between sheet resistance and the transparency

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Organic photovoltaic devices (OPD) using high conductive transparent few-walled carbon nanotubes (FWNT) film prepared by spraying was fabricated as a selective hole collection. Photovoltaic response with different sheet resistance ( $R_s$ ) and the transparency ( $T$ ) of FWNT film was investigated. Maximum efficiency of OPD up to 0.61% with the structure of FWNT ( $T=70\%$ ,  $R_s=86\ \Omega/\square$ )/poly(3-hexylthiophene): [6-6]phenyl- $C_{61}$ -butyric acid methyl ester/Al demonstrates a promising alternative of ITO (0.68%) with almost identical operation. The performance improvement results from the optimal balance between sheet resistance and transparency with three-dimensional network interface between nanotubes and polymers. © 2009 American Institute of Physics. [DOI: 10.1063/1.3103557]

Organic photovoltaic devices (OPDs) are being pursued as a viable alternative to inorganic devices due to low cost and scale-up production.<sup>1</sup> The conventional anode, indium tin oxide (ITO), bears a number of deficiencies including high temperature deposition and inflexibility. Recently, the focus shifts to the integration of carbon nanotubes (CNTs) thin film into OPD (Ref. 2) due to easy solution-processing fabrication and high flexibility. Single-walled CNTs (SWNT) films on glass or poly(ethylene terephthalate) (PET) were investigated.<sup>2,3</sup> Theoretically the work function of SWNT (4.8–5.0 eV) is sufficiently high to ensure the hole collection leading to better photovoltaic response.<sup>4</sup> However the best device using CNTs anode<sup>3</sup> was still lower than that of ITO. Thus the balance between the transparency and sheet resistance is crucial to OPD optimization. Previous works were focused on the device using SWNT film with the specific transparency and sheet resistance.<sup>2,3</sup> No detailed reports emerged concerning the changing properties by different sheet resistance and the transparency of CNTs electrode. In this letter, a series of high conductive few-walled CNTs (FWNT) films were utilized as the electrode in bulk-heterojunction OPD. Results indicated OPD performance was dependent on the sheet resistance and transparency of FWNT electrode. Optimal OPD using FWNT film ( $T=70\%$ ,  $R_s=86\ \Omega/\square$ ) as a hole collective contact with the efficiency of 0.61% almost operated identically well to the devices using ITO (0.68%).

Highly purified FWNT (Ref. 5) was processed by gas oxidation,  $H_2O_2$  solution<sup>6</sup> and refluxed in hydrochloric acid (HCl). Transmission electron microscopy (TEM) images of FWNT with double, triple, quadruple, or quintuple walls (indicated by arrow) were shown in Fig. 1. Purified samples

were well dispersed in 0.1% sodium dodecyl sulfate via the ultrasonication. Five FWNT films with different transparency and sheet resistance were prepared by spraying. Uniform FWNT transparent film was obtained by the oxidation.

The variation in sheet resistance (Keithley four-probe measurements) versus the transparency (Varian Cary 500 UV-visible-Near-infrared spectrometer) at 550 nm (a) before and (b) after 2 h  $HNO_3$  treatment is plotted in Fig. 2.  $HNO_3$  treatment reduced the resistance dramatically with slight increase in the transparency due to the increase in the delocalized carrier density through intertube junction by the removal of surfactant using redox dopants.<sup>7</sup> FWNT films with  $R_s$  of 70, 86, and  $160\ \Omega/\square$  at the corresponding  $T$  of 60%, 70%, and 80% were obtained. Both two curves reveal the dependence of the decreased sheet resistance on the cost of the transparency. Importantly the tenfold decrease in

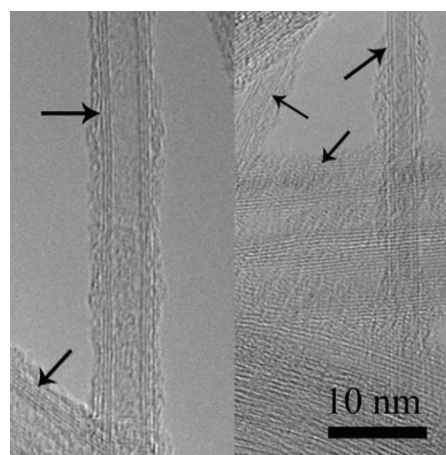


FIG. 1. TEM images of FWNT. Arrows indicate double, triple, quadruple, or quintuple side walls.

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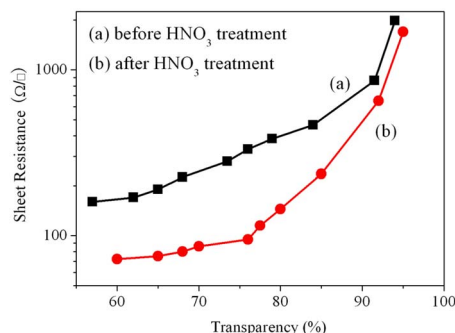


FIG. 2. (Color online) The variation in sheet resistance vs the transparency of FWNT film at 550 nm (a) before and (b) after 2 h  $\text{HNO}_3$  treatment.

resistance is accompanied with  $\sim 1.5$ -fold increase in the transparency. Therefore, it is critical to build the trade-off between sheet resistance and the transparency of FWNT anode for OPD optimization.

Figure 3 shows scanning electron microscope (SEM) (FEI XL30) images of the continuous FWNT film consisting of micron-length nanotubes parallel deposited on the substrate. Few remaining surfactant (white spot) on FWNT film lower the contact resistance among the cross-junction. Figure 4 shows the optical absorption spectra of (a) FWNT transparent film and (b) FWNT/poly(3-hexylthiophene) (P3HT):[6-6]phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM) film. FWNT mostly absorbs the light at the wavelength shorter than 360 nm. It is considered that a large portion of excitons at this region is surpassed by FWNT electrode. The solar cell of P3HT:PCBM showed high External Quantum Efficiency value of 350–600 nm quenching sharply at the wavelength shorter than 350 nm.<sup>8</sup> Thus light penetration to active layer of P3HT:PCBM mostly covers the wavelength of 350–650 nm.

FWNT transparent film was prepared on glass slide. P3HT and PCBM active layer was spin coated with annealing. Conjugated polymers were free to diffuse and fill in the open porosity of FWNT film.<sup>9</sup> Al top electrode ( $\sim 100$  nm) was evaporated under high vacuum. Figure 5 plotted the current versus voltage ( $J/V$ ) (Keithley 237 high voltage source generator under AM1.5 illumination) characteristic with P3HT:PCBM as active layer using FWNT film of (a) the transparency  $T=85\%$ , (b)  $T=80\%$ , (c)  $T=60\%$ , (d)  $T=70\%$ , and (e) ITO as the anode. Short current ( $J_{sc}$ ), open voltage ( $V_{oc}$ ), fill factor (FF), and efficiency ( $\eta$ ) were schemed in Table I. Generally, a trend of the characteristic improvement with the decrease in sheet resistance is indicated at high transparency.<sup>2</sup> This trend achieves the maximum at  $T=70\%$ . The optimal performance fabricated by FWNT ( $T=70\%$ ,  $R_s=86 \Omega/\square$ )/P3HT:PCBM/Al exhibits  $J_{sc}=4.46 \text{ mA}/\text{cm}^2$ ,  $V_{oc}=360 \text{ mV}$ ,  $\text{FF}=0.378$ , and  $\eta=0.61\%$ . This compares

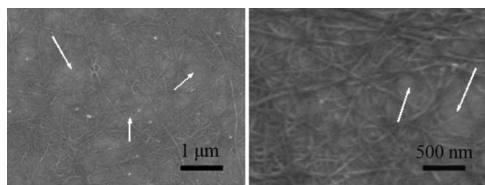


FIG. 3. SEM images of high conducting transparent FWNT film on glass slide. Arrows show the vacancy of the film infiltrated by polymers.

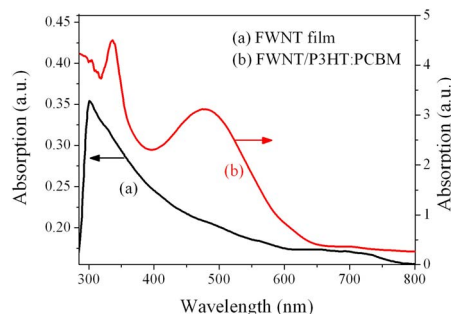


FIG. 4. (Color online) Optical absorption spectra of (a) FWNT transparent film and (b) FWNT/P3HT:PCBM film.

well the devices using ITO ( $\eta=0.68\%$ ) and surpasses the device without ITO and poly(3,4-ethylenedioxythiophene).<sup>2</sup> In addition, the device using FWNT electrode ( $T=60\%$ ,  $R_s=70 \Omega/\square$ ) shows slightly decreased properties ( $J_{sc}=4.34 \text{ mA}/\text{cm}^2$ ,  $V_{oc}=350 \text{ mV}$ ,  $\text{FF}=0.368$ , and  $\eta=0.56\%$ ) due to reduced light absorbing, different from the previous result showing best properties with the lowest resistance of  $282 \Omega/\square$  at  $T=40\%$ .<sup>2</sup> Results reveal low sheet resistance is fundamentally vital to the properties as well, and the transparency is also a considerable effect with a harvest of excitons creation. Therefore, the optimal balance plays a significant important role in devices improvement.

Optimal device using FWNT anode might be attributed to three-dimensional (3D) network of FWNT film. Conjugated polymers infiltrate the vacancy and porous FWNT network (black arrows in Fig. 3) when deposited on top. Intimate contact enlarges the interface between FWNT and photoactive polymers leading to efficient holes collection. The infiltration provides sufficient exposure of nanocomposites to the illumination.<sup>2</sup> This feature efficiently facilitates the exciton creation and dissociation at P3HT/PCBM interface. Therefore, in contrast to planar configuration of ITO, 3D network of FWNT film is beneficial to bulk heterojunction and contribute to the performance enhancement.

In conclusion, we fabricated organic cells using five FWNT films as holes collection. Photovoltaic performance varies from different sheet resistance and the transparency of FWNT electrode. Optimal efficiency up to  $0.61\%$  with the structure of FWNT ( $T=70\%$ ,  $R_s=86 \Omega/\square$ )/P3HT:PCBM/Al was obtained. The device identically compares well to the cells using ITO ( $0.68\%$ ). Results indicate that FWNT film is

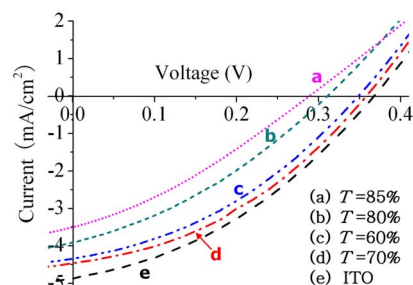


FIG. 5. (Color online) Current density vs voltage ( $J/V$ ) characteristic of OPD with P3HT:PCBM as active layer using FWNT film of (a) the transparency  $T=85\%$ , (b)  $T=80\%$ , (c)  $T=60\%$ , (d)  $T=70\%$ , and (e) ITO as the anode.

TABLE I. Current density vs voltage characteristic of OPD of FWNT (ITO)/P3HT:PCBM/Al with different sheet resistance and the transparency.

Devices structure	FWNT film		Photovoltaic characteristic			
	$T$ (%)	$R_s$ ( $\Omega/\square$ )	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)
ITO/P3HT:PCBM/Al	89	40	4.87	380	0.367	0.68
	60	70	4.34	350	0.368	0.56
FWNT/P3HT:PCBM/Al	70	86	4.46	360	0.378	0.61
	80	146	3.91	310	0.338	0.41
	85	235	3.50	290	0.315	0.32

a promising direct alternative to ITO for bulk-heterojunction OPD.

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