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# Efficient flexible polymer solar cells based on solution-processed reduced graphene oxide–Assisted silver nanowire transparent electrode

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ABSTRACT

It is reported a kind of solution-processible transparent conductive film consisting of reduced graphene oxide (rGO) nanosheets and silver nanowires (AgNWs). The sandwiched structure of rGO/AgNWs/rGO is readily deposited via layer-by-layer blade-coating on the rigid glass or flexible PET substrate at mild annealing temperature. The rGO nanosheets sandwiching the AgNWs networks not only induce close contact of the AgNWs networks as a clipper to improve the conductivity, but also link the discrete AgNWs as a connector to improve the uniformity of the film conductivity. The transparent rGO/AgNWs/rGO film exhibits sheet resistance as low as 14.29 Ω/□ with transmittance over 90% at 550 nm. Moreover, the rGO/AgNWs/rGO composite film shows good ambient stability due to the rGO coverage and the existing charge interaction between AgNWs and rGO. Polymer solar cells are fabricated on the transparent rGO/AgNWs/rGO-coated glass or flexible PET substrates and they exhibit comparable photovoltaic perfromance to the control devices fabricated on the commercial ITO substrate. More importantly, the PSCs based on the rGO/AgNWs/rGO/PET substrate show more excellent flexibility than that of the device based on the ITO/PET substrate.



## 1. Introduction

Transparent conductive electrodes are one of the essential components in optoelectronic devices such as touch screens, thin-film solar cells, organic light-emitting diodes (OLEDs) and flat panel displays. Indium tin oxide (ITO) has been widely used in OLEDs and polymer solar cells (PSCs) due to its excellent optoelectronic properties. However, it is an undesirable material for the development of next-generation flexible optoelectronic devices because of the scarcity of indium and its inherent brittleness [1–10]. Several emerging materials including carbon nanotubes (CNTs) [11,12], graphene [13–16], metallic nanowires [17–22], and conducting polymers [23–27] have shown promise for the replacement of ITO films since they have the potential for large-area fabrication and some degree of mechanical compliance. Among these candidates, the silver nanowires (AgNWs)-based films hold great promise due to outstanding electrical and optical properties. More importantly, the AgNWs films can be deposited in solution onto the substrates allowing for integration with low-cost roll-to-roll fabrication of PSCs [24,28–30]. Although it is promising, the pristine AgNWs films always suffer several drawbacks including poor electrical contact, large contact resistance, non-uniform conductivity and poor ambient stability [8,31,32]. The junction contact among AgNW networks is a key factor on determining the final conductivity of the resultant AgNWs film. The welding at the contact junction of AgNW networks has been achieved by thermal annealing at a temperature range of 150–300 °C [33–35]. However, this approach may be not suitable for the AgNWs deposition on plastic substrate due to the deformation of plastic substrates at high temperatures. Recently, there are extensive researches on the transparent conductive films based on the randomly distributed graphene films or graphene-based composites [36–38]. While the solution-processed graphene film always suffers from poor optoelectric behaviour with a high sheet resistance of ~2000 Ω/□ and a transmittance of 85%. Stacked structure of graphene and metal nanowires was suggested to be promising alternatives to fabricate transparent conductive

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film [39–42]. The AgNWs were covered with a graphene layer by the chemical vapor deposition (CVD) and sheet resistance of the resultant film was effectively reduced [39]. Although the proposed procedure is difficult to realize with solution-processing, it is highlighted that the AgNWs/graphene hybrid structure is a promising candidate for the transparent electrode materials.

Herein, we report a kind of solution-processed transparent conductive film consisting of reduced graphene oxide (rGO) nanosheets and AgNWs. The sandwiched structure of rGO/AgNWs/rGO can be readily deposited through layer-by-layer blade-coating on the rigid glass or flexible poly(ethylene terephthalate) (PET) substrate at mild annealing temperature. The sheet resistance of the rGO/AgNWs/rGO film can be as low as 14.29 Ω/□ with the film transmittance over 90% at 550 nm. It is found that this kind of rGO/AgNWs/rGO sandwich structure may effectively push to close contacts of AgNW networks and hence improves the conductivity of the resulted film. Moreover, the rGO/AgNWs/rGO film exhibits improved ambient stability compared to the pristine AgNWs film possibly due to the package effect of rGO and the partial charge transfer from AgNWs to rGO as evidenced by the photoelectron spectroscopy. The rGO/AgNWs/rGO film is deposited on glass or flexible PET substrate and is employed as the transparent cathode to fabricate inverted PSCs. The PSCs employing the transparent rGO/AgNWs/rGO electrode exhibit comparable photovoltaic performance to the counterpart PSCs using ITO as the transparent cathode. The flexible PSCs employing the rGO/AgNWs/rGO electrode show more flexible stability than the PSCs fabricated on the commercial ITO/PET substrate, implying the possibility of the solution-processible rGO/AgNWs/rGO electrode to integrate with the roll-to-roll manufacturing of flexible PSCs.

## 2. Experimental

### 2.1. Materials

Graphite oxide was prepared from natural graphite power according to a modified Hummers method [43,44]. Branched poly(ethylenimine) (BPEI) (Mw = 25 000) was obtained from Aldrich and used as received. Reduced graphite oxide (rGO) was prepared from graphene oxide (GO) according to the reported method [43]. BPEI reduced graphene oxide (rGO) solution was attained by redispersing them in ethanol in 1 mg/mL. AgNWs were obtained from Blue Nano Inc. The poly[N-9″-hepta-decanyl-2,7-Carbazole-alt-5,5-(4′,7′-dithienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) was synthesized in our laboratory. Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-*b*; 4,5-*b*′]dithiophene-2,6- diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2−6-diyl] (PBDTTT-EFT) was purchased from 1-Materials Inc. [6,6]-phenyl $C_{71}$-butyric acid methyl ester ($PC_{71}BM$) was purchased from American Dye Source Inc. ZnO nanoparticles with a diameter of ca. 5 nm were prepared following the synthesis route reported by Beek et al. [45].

### 2.2. Preparation of the transparent rGO/AgNWs/rGO film

The rGO solution was deposited onto the pre-cleaned glass or PET substrates via doctor-blade coating at 20 mm/s and baked at 50 °C for 5 min to remove the solvent. The AgNWs dispersion with different concentration were then deposited via doctor blading at 60 mm/s with the substrate temperature kept at 50 °C during the coating process. The density of the AgNWs layer was varied by changing the concentration of AgNWs dispersion. Subsequently, a top rGO layer was deposited as the first step, and was repeated three times. The sheet resistance of the conductive films was measured by the four-point probe technique. Transmittance of the various films was recorded on a SolidSpec-3700 UV-VIS-NIR spectrophotometer equipped with an integrated sphere. Scanning electron microscope (SEM) images were obtained on Philips XL-30 ESEM.

### 2.3. Device fabrication and measurement

The PSCs were fabricated on the rGO/AgNWs/rGO-coated glass or PET substrates. The control devices were also fabricated on the ITO/glass substrate (10 Ω/□) and flexible ITO/PET substrate (31Ω/□). A 25-nm-thick ZnO layer was firstly spin-coated on the ITO or rGO/AgNWs/rGO substrate as the cathode buffer layer. The PCDTBT:$PC_{71}BM$ (1:4 in weight, 80 nm) active layer or PBDTTT-EFT:$PC_{71}BM$ (1:1.5 in weight, 100 nm) was spincoated on the ZnO layer. A structure of $MoO_3$ (12 nm)/Al (100 nm) anode was thermally deposited in vacuum chamber to complete the device fabrication. The active area for each device is ca.12.56 $mm^2$. The illuminated current density-voltage (J-V) curves were recorded with the devices illuminated under 100 $mW/cm^2$ simulated solar light. The external quantum efficiency (EQE) curves were recorded on Enlitech QE-R spectral response measurement system.

## 3. Results and discussion

The effects of AgNWs densities on the sheet resistance and

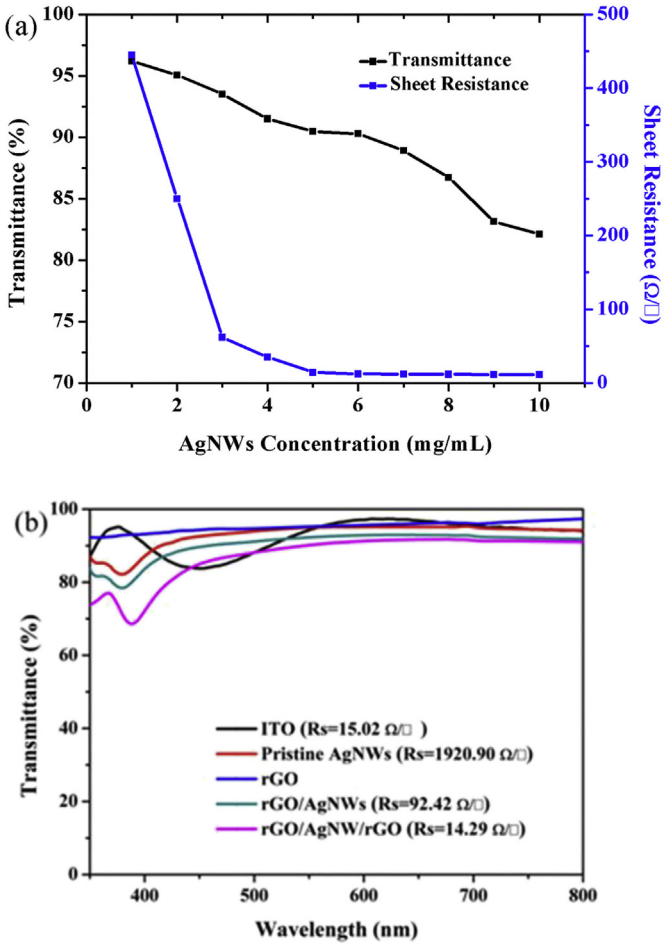


**Fig. 1.** (a) Transmittance at 550 nm and sheet resistance of the rGO/AgNW/rGO films prepared with different concentration of the AgNWs dispersion. (b) Transmittance spectra of the pristine AgNWs, rGO, rGO/AgNWs, rGO/AgNWs/rGO and ITO/glass substrate. The AgNWs dispersion with 5 mg/mL is used to prepare the AgNWs-based films.