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Ag-nanowire films coated with ZnO nanoparticles as a transparent electrode for solar cells

Frederik S. F. Morgenstern,[1,a)] Dinesh Kabra,[1] Sylvain Massip,[1] Thomas J. K. Brenner,[1] Philip E. Lyons,[2] Jonathan N. Coleman,[2] and Richard H. Friend[1]

[1]*Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB30HE, United Kingdom*
[2]*School of Physics, Trinity College Dublin, Dublin 2, Ireland*

We demonstrate that solution-processible silver-nanowire films coated with zinc-oxide-nanoparticles (ZnO-NPs) can be used as transparent electrodes in organic photovoltaic devices. The ZnO-NP coating acts as electron extraction layer and as encapsulating agent, protecting the wires from oxidation and improving their mechanical stability. Scanning photocurrent microscopy showed photocurrent generation to be more efficient at the active material surrounding the wires. Ultra-violet illumination as present in the solar spectrum was found to enhance photocurrent by improving the ZnO in-layer conductivity through the photoconductive effect. Inverted polythiophene:fullerene devices using ZnO-NP coated silver-nanowires or indium-tin-oxide as transparent electrode reached power conversion efficiencies of 2.4%. © 2011 American Institute of Physics.
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Organic photovoltaics[1] have attracted great attention in the past decade, not least because they may offer the advantage of low cost, large area roll to roll production.[2] Due to its high transparency of about 90%, whilst providing a low sheet resistance of about 15 $\Omega/\square$, indium-tin-oxide (ITO) has been the favored material for use as the transparent electrode in optoelectronic applications. While its optical and electronic properties are good, indium is relatively scarce and ITO is more expensive than desired. Transparent silver nanowire (Ag-NW) electrodes have recently attracted great interest as a possible candidate for photovoltaic applications.[3–6] Coleman *et al.*[7] showed Ag-NW films that reach high electrical to optical conductivity ratios of $\sigma_{DC}/\sigma_{opt} = 500$, similar to that of ITO, with transparencies of 85% at a sheet resistance of 13 $\Omega/\square$. Such Ag-NW based electrodes were found to be resistant to continuous bending, with no observed increase in sheet resistance after 1000 bending cycles at a curvature radius of 2.5 mm.[7] It has been shown that nanostructured thin films can be efficiently deposited at low temperatures by spray casting,[8] opening the way to cheap large area deposition of Ag-NWs. However, the high sensitivity to physical contact (the substrates fail to pass the scotch tape test[7]) as well as high mean roughness and non-conformal coverage of the substrate limit the applicability of untreated Ag-NW films. In this paper, we use solution processible ZnO nanoparticle (ZnO-NP) coated Ag-NW films as the electron-collecting electrode in organic hybrid solar cells. The typical device architecture of these cells is shown in Figure 1.

Ag-NW substrates used in this work were prepared according to the method reported by Coleman *et al.*,[7] with average Ag-NW dimensions of 6.5 μm length and 80 nm diameter. These Ag-NW films have a network structure with spacing between adjacent nanowires typically in the range of 2 μm-6 μm. Subsequently a 70 nm thick film of colloidal ZnO-NP ($\sim$5 nm diameter[9]) was spin-coated on top of the Ag-NW film. The substrates were then annealed for 30 min at 250 °C under an inert atmosphere. AFM images show a reduction of mean roughness (R_a) from about 42 nm for untreated Ag-NW films to about 10 nm for ZnO-NP coated substrates. ZnO-NPs were was found to completely cover the Ag-NW, forming a robust coating during thermal annealing (see thermal stability discussion below). The resulting Ag-NW:ZnO-NP showed an increased mechanical stability and passed the scotch-tape test. Sheet resistances (R_S) were obtained by measuring the resistance between two silver electrodes enclosing a 6 mm × 12 mm area of the Ag-NW film. The addition of the ZnO-NP layer onto the nanowire network caused a slight decrease in R_S from 4.8 $\Omega/\square$ to 4.2 $\Omega/\square$. Subsequently, the R_S of untreated and ZnO-NP coated Ag-NW substrates was studied as a function of annealing temperature. Substrates were placed on a hotplate and heated for 2 min at different temperatures, starting at 250 °C up to 370 °C in 20 °C steps. After each heating cycle, the substrates were cooled to room temperature and their R_S was measured. While ZnO-NP coated nanowire substrates heated up to 370 °C displayed only a slight increase in R_S from 4.2 $\Omega/\square$ to 5.0 $\Omega/\square$, untreated Ag-NWs substrates showed a 25 fold increase in resistivity for the same temperature and time range (Fig. 2 inset). This demonstrates that the ZnO-NP layer provides full encapsulation for the Ag-NWs. UV-Vis transmission spectra of Ag-NW substrates before and after ZnO-NP coating are shown in Fig. 2(b). In the visible and near infra-red spectrum (1100 nm > λ > 375 nm), the substrate transmittance is determined by the transmittance of the Ag-NW film T_{plain}, with variations in transmittance between coated (T_{coated}) and plain Ag-NW smaller than $\Delta T = T_{plain} - T_{coated} < 4\%$. The absorption of the ZnO-NP layer onsets at 375 nm, with a blue shifted absorbance peak at 338 nm (3.67 eV) when compared to bulk ZnO (370 nm or 3.35 eV). After annealing, a slight red-shift (6 nm) of the absorbance peak (344 nm or 3.61 eV) is observed,[9] consistent with some degree of nanoparticle sintering.

a)Author to whom correspondence should be addressed. Electronic mail: fsfm2@cam.ac.uk.
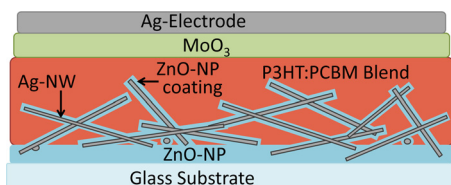
FIG. 1. (Color online) Device structure of a bulk heterojunction inverted solar cell using a ZnO nanoparticle coated Ag-NW film as the transparent electrode.

Photovoltaic devices using ZnO-NP coated Ag-NWs as transparent electrode were prepared as follows. Phenyl-C61-butyric acid methyl ester PCBM (Solenne) was used as the acceptor and regio-regular Poly(3-hexylthiophene-2,5-diyl) (Rieke Metals, $M_W = 87\,000$ g/mol, RR = 98%) as donor material (Fig. 1). A P3HT:PCBM blend was spin coated on top of the ZnO-NP:Ag-NW film substrates using a concentration of 44 mg/ml in chlorobenzene solution at a 1:1 weight ratio. AFM images showed P3HT:PCBM film thicknesses of about 400 nm for the nanowire system and about 250 nm for the ZnO-NP coated ITO substrates used as reference devices. We consider the variance in active layer thickness to arise from the inherent roughness of the Ag-NW film. Subsequently, a 10 nm thin hole extracting layer of MoO_3 was evaporated on top of the active layer. A 100 nm thick layer of silver was used as the top electrode. All devices were post-annealed for 5 min at 140 °C in nitrogen environment.

Device characteristics were taken under AM 1.5 conditions, using an ABET sun 2000 solar simulator. Open circuit voltages (V_{OC}) of 0.59 V and 0.61 V were measured for Ag-NW:ZnO-NP/P3HT:PCBM/MoO_3/Ag and ITO:ZnO-NP/P3HT:PCBM/MoO_3/Ag devices, respectively, in agreement with previously reported open circuit voltages of devices using similar architectures.[10,11] Lower values of V_{OC} were observed in some batches. This is possibly due to Ag-NWs tilted out of plane towards the top electrode, resulting in a lowered shunt resistance and V_{OC}. However, we consider that improved size control of the Ag-NWs can reduce the occurrence of such issues. The Ag-NW device showed a power conversion efficiency PCE = 2.4% and short circuit current density (J_{SC}) of 8.6 mA/cm^2 with a fill factor of

FF = 46%. ITO:ZnO-NP/P3HT:PCBM/MoO_3/Ag reference device showed almost no change in performance, having a PCE = 2.4%, J_{SC} = 8.5 mA/cm^2, and FF = 48%. We note that the literature reports of devices using similar architecture and ITO as the bottom electrode reached similar efficiencies,[10,12] demonstrating the applicability of Ag-NW films as an alternative to ITO.

UV light is well known to strongly affect the conductive properties of ZnO. This is especially the case for ZnO nanoparticles.[13] Sheet resistances were obtained under AM 1.5 condition in air using aluminium electrodes evaporated onto a 70 nm thick ZnO-NP layer, giving channel dimensions of 80 μm length and 3 mm width. A range of UV long-pass filters was used to measure the photoconductive response of the ZnO-NP at different wavelengths. Under AM 1.5 condition, sheet resistances were found to decrease by 5 orders of magnitude when compared to sheet resistances in dark (Fig. 3(a)), with $R_S(dark) = (5.5 \pm 1.1) \cdot 10^{14}$ $\Omega/\square$ and $R_S(light) = (3.6 \pm 0.6) \cdot 10^9$ $\Omega/\square$. Near-UV light ranging from 440 nm to 345 nm was found responsible for the decrease in R_S. To simulate the oxygen deprivation the ZnO layer encounters in photovoltaic devices, channels were then encapsulated using epoxy resin. Such ZnO-NP channels showed two orders of magnitude lower R_S than non-encapsulated channels and similar spectral response, with $R_S(dark) = (4.5 \pm 0.8) \cdot 10^{11}$ $\Omega/\square$ and $R_S(light) = (1.1 \pm 0.2) \cdot 10^7 \Omega/\square$.

Spectrally resolved external quantum efficiency (EQE) measurements were conducted on both Ag-NW and ITO based inverted structure devices. A 365 nm Spectroline ENF-260C UV lamp of 3 W/m^2 power intensity (about seven times less than the UV intensity of the solar simulator) was used as the UV doping source to account for the photoconductive effect of ZnO-NPs. Relative increases in EQEs during and after UV illumination were calculated with respect to the EQE measured before UV illumination at the peak wavelength of $\lambda = 525$ nm. For ITO and Ag-NW devices, a
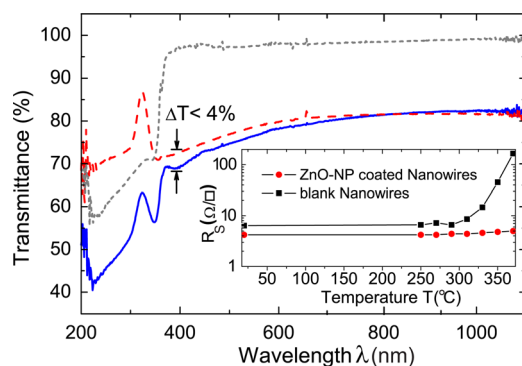

FIG. 2. (Color online) UV-Vis spectrum of Ag-NW substrates (dashed curve) and ZnO-NP coated Ag-NW substrates (solid curve). The dotted curve shows the UV-Vis spectrum of a plain 70 nm ZnO-NP film after annealing. Inset: sheet resistance measured at room temperature of both plain and ZnO-NP coated Ag-NW films after annealing for 2 min at increasing temperatures.
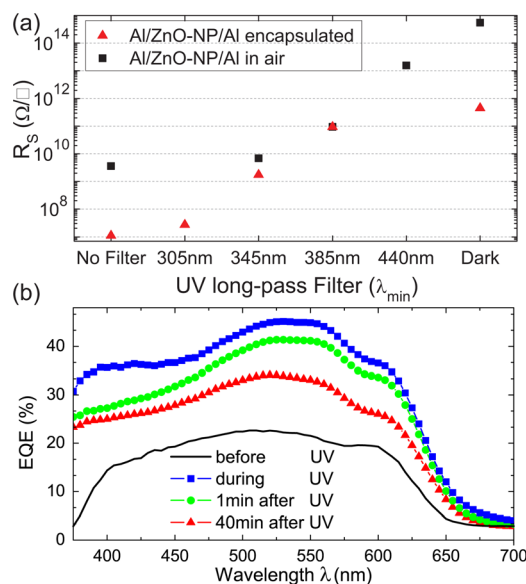

FIG. 3. (Color online) (a) Sheet resistance R_S of blank and encapsulated Al/ZnO-NP/Al channels measured under AM 1.5 conditions passed through different UV long-pass filters. (b) Spectrally resolved EQE of a AgNW:ZnO-NP/P3HT:PCBM/MoO_3/Ag device before, during, and after UV illumination using a 365 nm UV lamp at 3 W/m^2 power density.

respective increase in EQE of 50% and 100% was measured under UV illumination (Fig. 3(b)). Increased EQEs were measured up to 40 min after UV illumination. Under 365 nm UV-background illumination, the R_S of the non-encapsulated ZnO-NP layer ($R_S(365 \text{ nm}) = 3.9 \cdot 10^{12}$ $\Omega/\square$) is three orders of magnitude higher than R_S measured under AM 1.5 condition. EQEs under AM 1.5 conditions might therefore lie even higher. Ag-NW devices were found to be especially susceptible to changes in the conductivity of the ZnO-NP film. For ITO devices, charges reaching the PCBM:P3HT-ZnO interface must travel only 70 nm vertically to reach the collecting electrode. Charges injected in the ZnO layer of Ag-NW devices on the other hand have to travel distances of up to 2 μm horizontally to reach the next nanowire, resulting in considerable transport losses. An increase in conductivity of the ZnO layer is therefore expected to have a bigger impact on charge extraction efficiency of devices using Ag-NW than on ITO devices.

Confocal scanning photocurrent microscopy measurements[14,15] were performed to investigate the effect of in-plane conductance of the Ag-NW:ZnO-NP electrode on charge extraction at a microscopic length-scale. A 445 nm mechanically chopped Coherent CUBE laser (3 μW) was used as the probe beam and a 365 nm Spectroline ENF-260C lamp as the UV background source. Spatially resolved modulated photocurrent was measured with and without UV background exposure. The surface was imaged by two dimensional reflected luminescence mapping between 480 nm and 757 nm as shown in Figure 4(a). The effective extraction of photo-induced charges was found to be limited to the active material surrounding the nanowires (Fig. 4(b)). A factor five drop in photocurrent was measured between efficient regions with underlying nanowires and nanowire-free, dark regions, suggesting that the dark areas do not significantly contribute to photocurrent. During UV illumination, a linear increase in photocurrent of 100% was observed over the whole measured area (Fig. 4(c)). Interestingly, the increase in charge extraction efficiency was not only limited to regions far from the NW network but was also observed in the immediate vicinity of the wires, suggesting that charge injection from ZnO-NP layer into the Ag-NW is also improved upon photo-doping.

In conclusion, we present the use of solution processible Ag-NW film coated with ZnO-NP as an alternative to ITO electrodes for optoelectronic devices, particularly solar cells. UV illumination as present in the solar spectrum was found to increase the conductivity of ZnO-NP layers by five orders of magnitude, resulting in increased EQE under UV bias. Devices prepared using Ag-NW substrates showed similar device performance as the reference cells prepared on ITO substrates. The ZnO-NP coating acts as an efficient electron extraction layer, increases the substrates conductivity, and strongly improves the mechanical and thermal stabilities of Ag-NW film. Ag-NW films made of smaller nanowires (length and diameter) are expected to further improve the connectivity of the network and increase the photoactive regions without compromising the substrates transmittance, suggesting that solar cells using Ag-NW electrodes can match the performance of ITO cells.
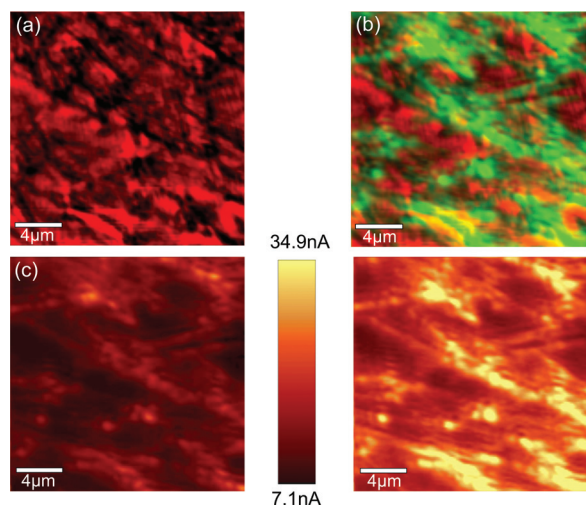
FIG. 4. (Color) (a) Two dimensional reflected photoluminescence of a Ag-NW:ZnO-NP/P3HT:PCBM/MoO$_3$/Ag device. Nanowires close to the surface appear dark (less reflection). (b) Superposition of reflected photoluminescence with the spatially resolved photocurrent of the same region. A correlation between nanowires (less reflective regions) and photoactive regions (green) is visible. (c) Scanning photocurrent microscopy images taken without (left) and with (right) UV backlight illumination of the same area.

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