Efficiency enhancement of organic solar cells using peroxo-polytitanic acid coated silver nanowires as transparent electrodes

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Solution-processed transparent electrodes made from silver-nanowires and peroxo-polytitanic (PPT) acid gel were developed for enhancing efficiency of organic solar cells. The electronic and optical properties of multilayer silver nanowires were significantly improved through the interconnection layers of amorphous titanium oxide (TiOx) from PPT acid gel. The AgNW–TiOx composite film showed averaged 92.14% optical transmittance with only 16.01 Ω sq−1 sheet resistance. Combining the transparent electrodes with poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PC61BM) blend, the efficiency of organic solar cells was 1.45 times that of devices using an ITO electrode. Optical simulations verified that the improvement was attributed to the enhanced near-field absorption and substantial scattering of incident light resulted from the random nature of the AgNW–TiOx core–shell nanostructure.

Recently, a solution-processed silver nanowires (AgNWs) mesh electrode was developed for bilayer solar cells with a comparable efficiency to that of cells with a commonly used metal-oxide electrode.18 However, the higher surface roughness of the AgNWs electrode leads to the possibility of inter-electrode shorting and thus poor device efficiency of less than 0.5% due to a higher leakage current. To overcome this problem, a thick layer (200 nm) of nano-particulate titania (TiOx) buffer layer was coated on AgNWs to reduce the nanowire rough surface.19 An improved PCE up to 3.5% was achieved due to a beneficial reduction of dark leakage current and a significantly increased photocurrent. The AgNWs with TiOx nanoparticles layer achieved 83% transparency at 550 nm and 15 Ω sq−1 sheet resistance. Its performance is comparable to their ITO counterpart.20

In this work, we developed a low cost-effective and convenient approach to fabricate ITO-comparable transparent electrodes by using a solution process of silver nanowires mixed with peroxo-polytitanic (PPT) acid gel. Different from the TiOx nanoparticles coating, the AgNW–PPT form core–shell nanostructures. The electrode has a higher transmittance of 93.7% at 550 nm, while remaining a low sheet resistance of 16.01 Ω sq−1. With the advantage of enhanced near-field absorption and substantial scattering of incident light resulted from the random nature of the AgNW–TiOx core–shell nanostructure, we achieved an average PCE of 4.69% in inverted polymer solar cells with this type of electrode. The efficiency is 36.7% improvement relative to that of reference devices with ITO electrode. Moreover, the composite electrode under mild thermal annealing can further reach a highest PCE of up to 5.05% due to an enhanced photocurrent generation resulting from the increased effective

Introduction

Polymer solar cells have attracted much attention due to the advantages of easy fabrication, larger-scale production, and good compatibility with flexible substrates.3–4 For the flexible devices, one of the most important issues is the exploitation of a transparent conducting electrode (TCE) with high transparency and low sheet resistance to replace the extensively used indium-tin oxide (ITO), which its fragility, incompatibility with flexible substrates.5,6
tand metal thin films have been investigated. However, the power conversion efficiencies (PCE) of devices with these alternative electrodes still cannot compete or even outstrip that of ITO both in theoretical calculations and experimental observations.7

Many possible candidate electrode materials, such as carbon nanotubes,6–8 graphene,9–11 conductive polymers,12–14 metal grids,15 and metal thin films have been investigated. However, the power conversion efficiencies (PCE) of devices with these alternative electrodes still cannot compete or even outstrip that of ITO both in theoretical calculations and experimental observations.7

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optical path length by the scattering from the annealing-induced Ag clusters.

**Experimental section**

**Device fabrication**

Inverted polymer solar cells were fabricated in a layer structure of glass/cathode/zinc oxide (ZnO)/poly[(3-hexylthiophene)-(6,6)-phenyl-C61-butyric acid methyl ester (P3HT:PC_{61}BM)/molybdenum oxide (MoO_{3})/Ag (cathode: AgNWs with or without PPT, ITO (Merck Inc., 24 Ω sq\(^{-1}\)) as the reference device). Silver nanowires (1.0 wt% in ethanol) with a diameter of ~35 nm and length of ~15–25 μm were purchased from Blue Nano Inc. After dilution to 0.2 wt%, the AgNW dispersion was spin-coated onto pre-cleaned glass substrates at 2000 rpm for 30 s. A yellow transparent PPT acid gel was prepared by mixing 60 μl of titanium isopropoxide (TTIP) (Sigma-Aldrich, 97%), 430 μl of hydrogen peroxide (H_{2}O_{2}) (Acros Organic, 97%), and 9.51 ml of H_{2}O, followed by continuously stirring for 48 hours at room temperature (RT). The resulting PPT acid gel was diluted in isopropyl alcohol to obtain the PPT coating solution. The PPT coating solution was then spin-coat onto the AgNW-coated glass substrates at 2000 rpm for 60 s, followed by air drying for 2 min. To match with the lowest unoccupied molecular orbital (LUMO) of PC_{61}BM and obtain a smooth electrode surface, a ZnO layer was coated on the AgNW layer. The layer was made by a 0.46 M of ZnO precursor solution dissolving equimolar zinc acetate dehydrate (Alfa Aesar, 98%) and monoethanolamine (Sigma-Aldrich, 99%) in 2-methoxy ethanol (Sigma-Aldrich, 99.8%). The prepared ZnO precursor solution was spin-coated onto the as-deposited AgNW–TiO_{2} composite film at 5000 rpm for 60 s. The amorphous ZnO films were then air annealed at 200 °C for 1 h. Subsequently, the active layer was cast from a solution containing 1.75 wt% P3HT:PC_{61}BM (Uni-Onward Corp., >99.5%) [1 : 1, w/w] in 1,2-dichlorobenzene at 800 rpm for 60 s inside N_{2} filled glove box. The photo voltaic layer was left in a glass Petri dish at RT for 60 min for slow solvent evaporation, and then thermally annealed at 170 °C for 10 min to obtain a ~220 nm-thick active layer. The devices were completed after thermal evaporation of MoO_{3} (10 nm) and Ag (100 nm) through a shadow mask under pressure of 6 × 10^{-6} Torr, giving an active area of 0.04 cm\(^2\) defined by the overlap between the patterned AgNW (or ITO) and top Ag contact. We defined the pattern of silver nanowire electrode by first sticking Scotch tape onto the AgNWs coated glass substrate and then removing the redundant part by tearing away the tape. The ITO electrode was made by chemically etching ITO glass through a tape mask with acid and alkali resistance. The AgNW electrode and ITO had the same 2 mm-wide conductive strip. For the ITO reference device, all processing conditions, except for not using TiO_{2}, were kept the same as for the AgNW-based one.

**Optical and electrical characterization**

The current density \(J\)-voltage \(V\) characteristics of devices were performed within a N_{2} filled glove box through a semiconductor parameter analyzer (HP 4145C) in the dark and under a simulated AM 1.5G spectrum provided by a Xenon lamp-based solar simulator (thermal Oriel 1000W) with a light intensity of 100 mW cm\(^{-2}\), calibrated through a silicon photodiode. The transmittance and reflectance spectra were recorded using an ultraviolet-visible spectrophotometer (Jasco V-550) with an integrating sphere reflectance accessory. The sheet resistance was measured using the four-point probe system and the average value was taken from at least 5 different locations. The film thickness was evaluated using a V- VASE variable-angle spectroscopic ellipsometer (J. A. Woollam Inc.). The optical modeling of the devices was performed using the finite element method (FEM) with the use of the software Comsol Multiphysics. The surface roughness and topography of electrodes were imaged by tapping mode atomic force microscopy (AFM) (Veeco di Inna SPM), and the surface morphology images were investigated by scanning electron microscopy (SEM) (LEO-1530 FEG SEM).

**Results and discussion**

**Optical, electrical properties and surface morphology**

Fig. 1(a) shows a schematic diagram for the fabrication of AgNW–TiO_{2} composite films. First, the AgNWs were spin-coat on the pre-cleaned glass substrate and presents a loose-packed structure. After spin-coating of the PPT coating solution onto the AgNWs and subsequently drying to remove the residual solvent at RT, the peroxo-polytitanic acid gel covers the surface of nanowires and distributes randomly in the openings of the crossed network. This gives rise to meniscus nanostructures around crossed AgNW positions and between the substrate and AgNWs due to capillary forces from solvent evaporation. The resulting AgNW–TiO_{2} core–shell nanostructures facilitate the enhancement of contacts between AgNWs and the adhesion of AgNWs to the underlying glass substrate. The thickness of TiO_{2} film was analyzed using ImageJ software from a TEM image of the selected area (Fig. 1(b)) and determined to be 1.82 ± 0.25 nm.

In Fig. 2, the sheet resistance and optical transmittance was investigated by measuring four different transparent conducting films: bare AgNW mesh, AgNW–TiO_{2} composite film without thermal annealing, AgNW–TiO_{2} (*) with thermal annealing at 150 °C under vacuum for 10 min, and ITO. The bare AgNW mesh showed 22.99 ± 2.02 Ω sq\(^{-1}\) sheet resistance and 91.77% transmission at 550 nm, as shown in Fig. 2(b). Upon lamination of TiO_{2} thin film onto AgNWs, the sheet resistance was substantially reduced to 16.01 ± 0.81 Ω sq\(^{-1}\) due to fusion at the contact of the nanowires which led to the reduction of contact resistance between the nanowires, and the transmittance was increased to 93.7% at 550 nm. This is attributed to the plasmonic effect of high refractive index (>2) TiO_{2} filler placed in the empty space in the crossed AgNW network. This extraordinary optical transmission improvement is seen near the 350 nm wavelength corresponding to the plasmonic absorption of the AgNWs, as can be seen in Fig. 2(a). After being treated with TiO_{2} sol-gel solution and further annealing, the resulting annealed AgNW composite films have an average transmittance of 89.21% from 350 to 800 nm with sheet resistance of 15.79 ± 0.15 Ω sq\(^{-1}\), which met the
The additional thermal annealing would further result in the formation of silver fusion at the contact of nanowires. The silver fusion formed larger Ag clusters and thus increased the scattering and absorbance of the incoming light. Therefore, the optical transmittance was decreased after thermal treatment. The sheet resistance of the ITO film was 24.05 ± 0.04 Ω sq⁻¹ and the transmittance was 89.11% at 550 nm.

In order to verify the composite film suitable for transparent conducting electrode of device, the surface morphology and topography of AgNW-based film was investigated by SEM and AFM. Fig. 3 shows the SEM images of a pristine AgNW network and AgNW–TiOₓ composite film with thermal annealing. The SEM image of Fig. 3(a) indicates that the AgNWs formed a uniform mesh with 28% cover ratio area analyzed by ImageJ software across the substrate. Upon lamination of TiOₓ onto nanowires, most of the TiOₓ film is centered largely in the cross-nanowire junctions which help strengthen the electrical contact between the nanowires and along edges of the nanowires, however, a few are randomly distributed in the openings between nanowires, as seen in the Fig. 3(b). Due to the lack of a supporting layer to fill the voids between neighboring nanowires, a further coating layer of amorphous ZnO onto AgNW–TiOₓ composite film is necessary for charge extraction and transportation and surface smoothing. Fig. 3(c) and (d) show that the AgNW and composite networks are completely buried in the ZnO material and the sharp edge of the original AgNW image appeared blurred. We also examined the surface topography using AFM because the surface roughness of the electrodes is closely interrelated with the cell-performance. Fig. 4 shows an AFM topographical image of bare AgNW mesh and AgNW–TiOₓ composite film with thermal annealing before and after ZnO coating. The fabrication process of bare AgNWs film was conducted by repeatedly spin-coating the AgNW solution on the glass substrate followed by drying at RT. Due to the incomplete removal of solvent at RT, the bare AgNWs film had a loose-packed structure. After thermal annealing, the film volume shrunk due to solvent evaporation and eventually formed a compact film structure. The annealing process would result in Ag clusters at the contact of nanowires, which increased the roughness at localized area. For the case of...
AgNW–TiO$_x$ composite, the TiO$_x$ filled at the openings between the crossed networks of AgNWs. It substantially decreased the surface roughness. Therefore, the root mean square (RMS) roughness of AgNW–TiO$_x$ composite film was significantly reduced to 23.52 nm relative to the surface roughness of the bare AgNW network (36.29 nm). The average height of the stacked nanowires (64.6 nm) decreased to half of that of the bare nanowire mesh (121.44 nm), which confirms the functionality of surface smoothing of TiO$_x$, as seen in Fig. 4(a) and (b). However, there still are sharper edges and ridges observed in

**Fig. 3** SEM images for (a) uncoated and (c) ZnO-coated bare AgNW mesh and for (b) uncoated and (d) ZnO-coated AgNW–TiO$_x$ composite film with thermal annealing. A 52° tilted SEM image was also shown in the inset.

**Fig. 4** AFM topography images for (a) uncoated and (c) ZnO-coated bare AgNW mesh and for (b) uncoated and (d) ZnO-coated AgNW–TiO$_x$ composite film with thermal annealing. The height profiles shown in insets are taken along the white double-headed arrows.
the height profile of insets. After being covered by a ZnO layer, the RMS and the average height of composite films was further reduced to 15.42 nm and 52 nm (Fig. 4(d)). Though the RMS value of AgNW-based film is relatively high compared to the ITO surface, the use of 220 nm thick active layer can effectively decrease the possibility of inter-electrode shorting and thus increase the device yield.

Device performance

To demonstrate the application of AgNW-based composite film in polymer solar cells, they were incorporated into devices with an inverted device configuration, as seen in the inset of Fig. 5(a). The reference device was made with the commercially available ITO-coated (100 nm) glass substrate as the transparent electrodes. The ZnO layer inserted in between the cathode and the active layer can serve as a buffer layer to smooth out the roughness, to match the work function and the RMS and the average height of composite films. The ZnO layer is relatively high compared to the ITO layer, which is consistent with the measured result in an ITO device, which is reasonable assuming 70% of internal quantum efficiency (IQE) for AgNW-based electrodes can capture more light than that of ITO devices as seen in Fig. 5(b). It can be seen that the devices with AgNW- and ITO electrode illuminated from the substrate side, measured the total absorption of AgNW–TiOx composite electrode at 570 nm for TM polarization is shown in Fig. 6(b). A comparison between these two contour plots clearly shows a broad, rather flat shape of the spectral response at wavelength range.

Simulations

To clarify the enhanced device absorption behavior originating from the combined effect of light scattering and plasmonic absorption of AgNW–TiOx core–shell nanostructure, we also conducted numerical simulations of the external quantum efficiency (EQE) spectra of the devices with AgNW–TiOx and ITO electrode (reasonably assuming 70% of internal quantum efficiency). In Fig. 6(a), the simulated EQE of a device with a composite electrode was significantly enhanced over a wide spectral region from 450 to 650 nm, and the maximum EQE value increased from 52% to 66.87% at 570 nm relative to that of an ITO device, which is consistent with the measured result in the inset of Fig. 6(a). For the transverse magnetic wave (TM) illumination, there is an observed dip ascribed to the absorption of Ag near 400 nm due to the excitation of localized surface plasmon resonance (LSPR); for the transverse electric wave (TE) illumination, there is no LSPR effect and the EQE spectrum shows a broad, rather flat shape of the spectral response at visible light range. Finally, the simulated power absorbed per unit volume of the overall device with AgNW–TiOx and ITO electrode at 570 nm for TM polarization is shown in Fig. 6(b). A comparison between these two contour plots clearly
demonstrates stronger power absorbed in the photoactive layer was obtained in the nanowire device rather than in the ITO device. Moreover, for the nanowire device, the maximum absorption concentrate underneath the protrusion of Ag nanowire, which can be attributed to the LSPR effect and thus lead to enhancement of the photocurrent. In contrast, the referenced ITO device did not produce a significant plasmonic field enhancement.

Conclusions

In summary, we have successfully improved the optical and electrical performance of AgNW-based transparent electrodes by using an interconnection layer of TiO$_x$ from PPT acid gel. With a further coating layer of amorphous ZnO onto AgNW–TiO$_x$ composite film, significant enhancement of the solar cell performance with a PCE of 4.69% was demonstrated as compared with 3.43% of an ITO reference device. The efficiency enhancement is attributed to the increased FF and $J_{sc}$ originating from surface plasmon resonances that lead to a strong near field enhancement as well as highly efficient light scattering as verified by the optical simulation. The applications of this newly developed TCE on OPVs offer great potential for the fabrication of high performing plastic solar cells.

Acknowledgements

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Notes and references


Table 1  Device performance parameters of the OPVs under 100 mW cm$^{-2}$ AM 1.5G illumination

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>PCE (%)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNW</td>
<td>0.58 ± 0.01 (0.58)$^a$</td>
<td>12.47 ± 0.24 (12.46)</td>
<td>4.45 ± 0.14 (4.63)</td>
<td>61.86 ± 2.17 (64.05)</td>
</tr>
<tr>
<td>AgNW–TiO$_x$</td>
<td>0.58 ± 0.01 (0.57)</td>
<td>13.32 ± 0.04 (13.6)</td>
<td>4.69 ± 0.05 (4.72)</td>
<td>61.23 ± 0.41 (60.94)</td>
</tr>
<tr>
<td>AgNW–TiO$_x$ (*)$^b$</td>
<td>0.58 ± 0.01 (0.58)</td>
<td>13.91 ± 0.93 (14.31)</td>
<td>4.98 ± 0.11 (5.05)</td>
<td>61.49 ± 2.28 (60.83)</td>
</tr>
<tr>
<td>ITO</td>
<td>0.58 ± 0.01 (0.57)</td>
<td>10.95 ± 0.06 (11.01)</td>
<td>3.43 ± 0.07 (3.5)</td>
<td>54.41 ± 1.00 (55.71)</td>
</tr>
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$^a$ The best-performing cell. $^b$ Composite film under thermal annealing at 150 ºC for 10 min.

Fig. 6  Numerical simulation results showing (a) the simulated external quantum efficiency (EQE) spectra of the devices with AgNW–TiO$_x$ and ITO electrode and (b) the power absorbed per unit volume in the cells at normal incident wavelength of 570 nm for the TM polarization. The measured EQE spectra are shown in the inset of (a).