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Waveguide effect enhancement of local photocurrent in hybrid organic/inorganic solar cells

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Abstract

The local efficiency of hybrid ZnO-nanorods/C₆₀/ZnPc:C₆₀/MoO₃/Ag solar cells, with different nanorods length has been investigated by scanning near-field optical microscopy. Simultaneous spatially resolved measurements of topography and photocurrent suggest a waveguide effect enhancement of the local photocurrent. This interpretation is supported by finite element method simulations of the light propagation in the solar cell.

Keywords: hybrid solar cells, fullerene C60, zinc phthalocyanine (ZnPc), ZnO-nanorods, scanning near-field optical microscopy, waveguide effect

1. Introduction

Because of their low cost, mechanical flexibility and light weight, hybrid organic/inorganic solar cells are very promising for applications in photovoltaic devices [1–4]. They are prepared by combining organic semiconductors [5] and inorganic nanostructures [6]. One type of nanostructures used in these solar cells are one-dimensional nanomaterials, i.e. nanowires or nanorods (NRs), because of their numerous advantages such as increased active area, high carrier mobility, thermal and ambient stability, and providing a direct path for charge transport [4, 7].

Several characterization techniques such as photoluminescence and electroluminescence [8], scanning Kelvin-probe microscopy [9–11], photoconductive atomic force microscopy [9–12] and near-field cathode-luminescence characterization methods [13] have been used to study the physical and optical properties of solar cells. In addition, the local photocurrent in solar cells [14–16] has been investigated using scanning near-field optical microscopy (SNOM). In SNOM, a tapered optical fiber probe, with a nanometric aperture at the tip, scans the surface of a sample while illuminating the sub-wavelength area under the probe aperture. The tip is kept at a distance of less than 10 nm from the

surface allowing the illumination of the sample in the region of the evanescent field. Thus, the properties of the surface can be studied with an optical resolution better than the diffraction limit of the incident light and enable simultaneous measurements of the surface topography and the optoelectronic properties of the sample.

We apply in this work the SNOM microscopy for studying hybrid organic/inorganic solar cells consisting of zinc oxide nanorods (ZnO-NRs) and small organic molecules. Notice that short-circuit current densities of 11.2 mA cm^{−2} were demonstrated on the latter devices in our previous work [4]. Even higher photocurrents on devices with longer NRs are expected due to a corresponding increase of the absorber active area. A further increase in photocurrent is expected because of higher transmittance and lower reflectance of the NRs compared to their planar counterparts. In the wavelength range of 400–800 nm the transmittance of the investigated ZnO-NRs is on average higher than 83% and thus surpassing that of the planar indium tin oxide (ITO) (5Ω/□) and ZnO:Al (5Ω/□) thin films which show a transmittance of 82% and 81%, respectively. In addition, ZnO-NRs show in the same wavelength range the lowest average reflection of about 7% [4]. Thus, NRs with improved optical properties and length should result in photovoltaic devices with higher power

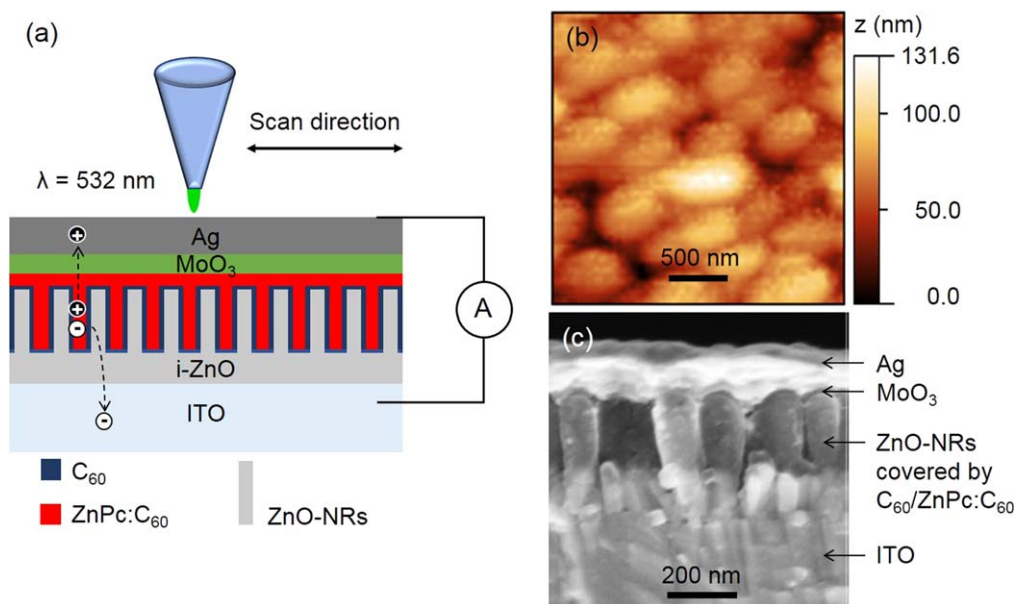


Figure 1. (a) Illustration of the hybrid solar cell device structure (cross section) under a near-field illumination. (b) Topography map obtained with SNOM. The color scale indicates the height variations, z . (c) Cross section view of the sample obtained by SEM.

conversion efficiency due to the enhanced short-circuit current density observed above. However, the effect of NRs with different length and the local photoactivity at the absorber/NR interface was so far not investigated by direct methods, e.g. such as SNOM. We performed therefore spatially resolved measurements of the photocurrent using the latter technique. We investigate the photocurrent distribution for three different samples with three different lengths of ZnO-NRs at an illumination wavelength of $\lambda = 532$ nm. We reveal by means of SNOM an additional beneficial optical effect, namely waveguide effect, resulting from the use of ZnO-NRs in combination with the ZnPc:C₆₀ blend absorber layer. As a consequence of the observed waveguide effect, higher photocurrents are observed in regions between the NRs. This interpretation is supported by simulations of the light propagation in solar cells using the finite element method (FEM). The investigations by SNOM revealed spatially dependent photoactivity of the PV device which is investigated in this study as a function of ZnO-NR lengths.

2. Experimental details

We used a home-built SNOM to measure topography and photocurrent of the samples simultaneously. Modulated monochromatic light ($\lambda = 532$ nm) was injected into a single-mode optical fiber (figure 1(a)), which is tapered at the extremity to form a cone-shaped tip (acquired from LovaLite, Besançon, France). The tips are coated with aluminum, leaving a nanometric aperture at the end playing the role of a 'nano-source' of light (100 nm aperture). The tip was firmly glued onto a tuning fork. The local photocurrent generated by the sample when illuminated through the tip aperture was detected with a lock-in amplifier (Princeton Applied Research, Oak Ridge, TN, USA). The topographic

information is measured with a second lock-in amplifier (Signal Recovery, Oak Ridge, TN, USA) by detecting the shear forces resulting from the interactions between tip and sample surface, via a tuning fork feedback system.

The samples investigated are hybrid organic/inorganic solar cells, which contain ZnO-NRs and a dry-processed small-molecule organic absorber consisting of a blend of zinc phthalocyanine (ZnPc) as donor and fullerene C₆₀ as acceptor. Under illumination, excitons are generated in the donor material. The excitons diffuse to the donor/acceptor interface and dissociate there in free electrons and holes. The free holes are then transported via the donor ZnPc to the MoO₃/Ag top contact, while the electrons are transported via the C₆₀ acceptor domains, C₆₀ layer and ZnO-NRs to the transparent ITO back contact. The ohmic contact at the ZnO/C₆₀ interface is realized by matching ZnO-NRs work function to the work function value of C₆₀ [4]. The effective charge selectivity for holes at the interface between ZnPc:C₆₀ blend layer and Ag top contact is ensured by the insertion of molybdenum oxide (MoO₃) layer at this interface.

Figure 1(a) shows a cross section schematic of the sample. ITO substrates were first covered by a seed layer of 30 nm sputtered intrinsic ZnO (i-ZnO). The ZnO-NRs were then grown by electrodeposition on ITO substrates from an aqueous solution of 5 mM Zn(NO₃)₂ and 5 mM NH₄NO₃ at a temperature of 75 °C. The ZnO-NRs diameter and length were adjusted by varying the deposition time [17, 18]. We investigated three samples with different ZnO-NR lengths of 154, 284 and 615 nm obtained after a deposition time of 400, 700 and 1500 s, respectively. Organic materials were deposited by a dry organic vapor phase deposition method [19, 20]. At first, a 25 nm C₆₀ layer was deposited on the ZnO-NRs. Subsequently, a 150 nm blend layer of ZnPc:C₆₀ was deposited as an absorber thin film on the C₆₀ layer. Then, a 10 nm layer of MoO₃ was evaporated on the ZnPc:C₆₀ blend

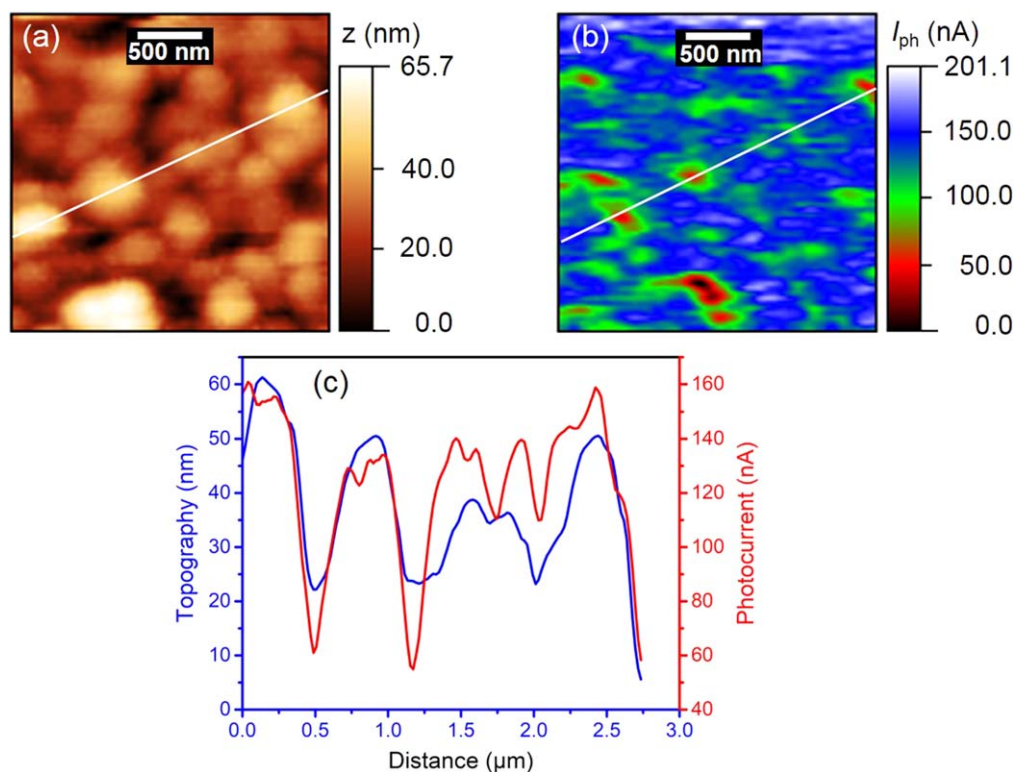


Figure 2. (a) Topography and (b) photocurrent (I_{ph}) maps measured simultaneously with SNOM. The color scales indicate the height variations, z , on topography and the I_{ph} magnitude on photocurrent maps, respectively. (c) Profiles of the topography and the photocurrent were taken along the white lines shown in (a) and (b).

layer. Finally, a 50 nm silver (Ag) layer was deposited as a top electrode. The topography of the surface of a complete solar cell device measured by SNOM is shown in figure 1(b). The device cross section is shown in the scanning electron microscopy (SEM) image in figure 1(c). A brief description of the optical properties of the investigated ZnO-nanorods and the photovoltaic performance of similar solar cell devices were given in the introduction. Further details can be found in [4].

3. Results and discussion

Figures 2(a) and (b) show the simultaneously recorded topography and photocurrent maps ($2.5 \times 2.5 \mu\text{m}^2$) measured simultaneously with SNOM from a solar cell containing ZnO-NRs with a length of 154 nm. The topography map in figure 2(a) contains bright areas that are related to the top of the ZnO-NRs and dark areas corresponding to the space between NRs. The corresponding photocurrent map in figure 2(b) is characterized mainly by regions of high current (blue) and regions of low current (green and red). It appears that the high photocurrent is produced on top of the ZnO-NRs, while the space in between generates less photocurrent. This is highlighted by the line profiles in figure 1(c) extracted at the same position from the topography and photocurrent maps. The curves show clearly that the local photocurrent values are higher on top of the ZnO-NRs than in the space in between. This behavior has also been recorded for the two

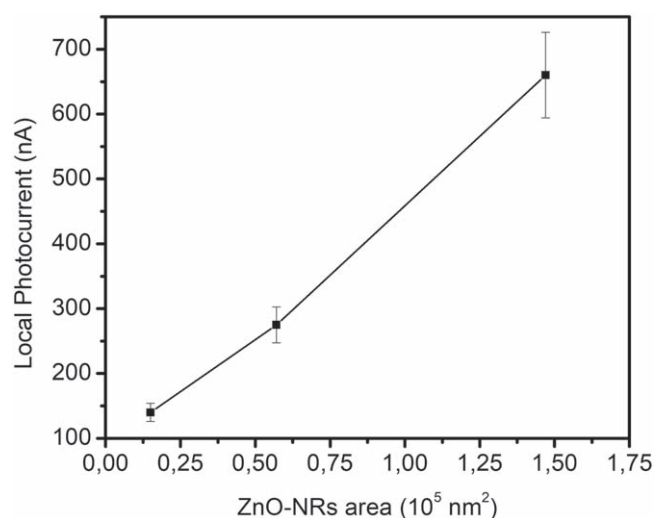


Figure 3. Local photocurrent behavior as a function of the ZnO-NRs area. Markers correspond to the actual measurements; the solid line is a guide for the eye. The error bars are obtained by measuring the roughness in the SNOM images.

other solar cells with ZnO-NR length of 284 and 615 nm. In addition, the local photocurrent appears to increase when the ZnO-NR length increases.

Figure 3 shows the evolution of the average photocurrent over a region of $25 \mu\text{m}^2$ as a function of the ZnO-NR area, where an increasing behavior is observed.

To understand the relationship between the length of ZnO-NRs and the magnitude of the photocurrent, the light

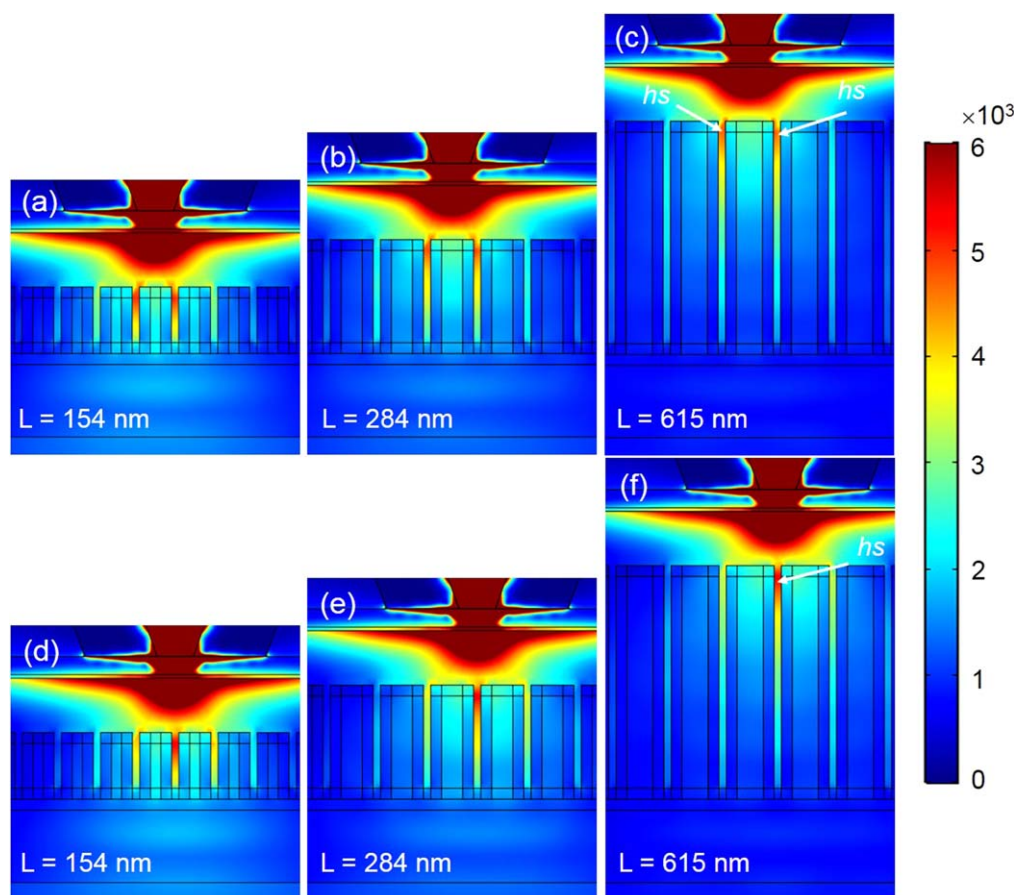


Figure 4. 2D simulated electric field amplitude for solar cells with different ZnO-NR length, L , and for different positions of the SNOM tip: (a)–(c) on top of a ZnO-NR; (d)–(f) above the inter-NRs space. The hot spots are denoted by *hs*.

propagation in the solar cell was simulated by FEM. Our FEM simulations are performed using the software package COMSOL Multiphysics™ in 2D. We calculate the electromagnetic field distribution with the response of the linear model to the harmonic excitation for one frequency. For all simulations, the overall box size is $2\ \mu\text{m} \times 4\ \mu\text{m}$ with an additional rectangular 300 nm perfectly matched layer system as the boundary. The maximum mesh size is 30 nm. The tip has an aperture of 100 nm in diameter and an aluminum coating of 200 nm in thickness. The incident light is a continuous wave at 532 nm with the power of 1 W. The geometry of the sample used for the simulation is depicted in figure 1(a). For simplicity, we consider an ordered ZnO-NRs array with an inter-NRs distance of 80 nm. The latter value was chosen in order to preserve the same thickness of the C_{60} layer (30 nm) on both sides of each ZnO-NR and to ensure the presence of the blend organic layer in the inter-NRs space. The following input parameters entered the simulation: the refractive indices (n) of the component materials $n_{\text{Ag}} = 0.13$ [21], $n_{\text{ZnPc}} = 1.43$, $n_{\text{C}_{60}} = 2.24$, $n_{\text{MoO}_3} = 2.2$ [22], and $n_{\text{ZnO}} = 1.88$ [23], the ZnO-NR length (L) and diameter (d) in nanometers as determined from the SEM images are: (L ; d) = (154; 28), (284; 58) and (615; 72). To simulate the change of the electromagnetic field distribution during tip scanning, the tip is set at different positions relative to the

nanorods array: above the center of one NR, and above the center of the pitch between two NRs.

Figure 4 shows the simulated electric field behavior in three different solar cells with different ZnO-NR length $L = 154\ \text{nm}$ (figures 4(a) and (d)), $L = 284\ \text{nm}$ (figures 4(b) and (e)) and $L = 615\ \text{nm}$ (figures 4(c) and (f)). It elucidates how the light is coming out of the SNOM tip, which is in contact with the solar cell's top surface, propagates through the different solar cell layers. The 2D simulation clearly indicates that the SNOM tip aperture is creating two hot spots (highlighted with 'hs' in figure 4(c)) and two waveguide channels on either side of the NR when it is on top of a NR. It is also important to point out that in a more realistic case (3D case), at least four hot spots and four waveguide channels would be excited on the different sides of the NR. Only one hot spot and one waveguide channel are generated when the tip aperture is in between two NRs (figure 4(f)). In a 2D geometry (figure 4), a nanorod is surrounded by only two neighboring NRs. The 2D simulation shows two generated waveguides: one to the left and another one to the right side of the NR. In a 3D geometry (the realistic case), a NR has four close neighbors. Thus, when the SNOM tip illuminates the top of a NR, four waveguide channels are excited. These channels surround the NR from four sides: left, right, front and rear. The electromagnetic hot spots are excited because of the increased amount of scattered light at the edge of the ZnO-

NRs top end. As mentioned above, the excitons are generated in the ZnPc (donor material) and dissociate after diffusion at the interface ZnPc/C₆₀ (donor/acceptor). The effect of a waveguiding in the narrow channel between two NRs combined with the hot spots leads to an enhancement of light absorption by the solar cell, and hence the generation of more excitons. When the tip is on top of a NR, more hot spots and more waveguiding channels are generated. It results in a higher enhancement of light absorption in comparison to the situation when the tip is illuminating the space between two NRs. Thus, the amount of local photocurrent produced when the SNOM tip illuminates the top of a NR is higher than the amount of local photocurrent produced if the tip is positioned between two NRs. The distance between NRs is smaller than the absorber thickness, as shown in the device cross section in figure 1(c). Therefore, the charge collection along a direction perpendicular to the NRs is much more effective.

The simulation shows also that the coupling between light and ZnO-NRs leads to a waveguide effect in the ZnO-NRs [24, 25]. However, the latter effect is weaker than the waveguide effect in the channel between two NRs and yet it can contribute to improving the photocurrent. In fact, ZnO has the largest energy gap of the solar cell constituents and does not absorb the light. Therefore, the light might reach the organic layer easily, which further increases the photocurrent.

Thus, when the SNOM tip is on top of a NR (figures 4(a)–(c)), the effect of two electromagnetic hot spots combined with the waveguide effect in the two channels on either side of NR and the waveguide effect in the NR itself are responsible for the high photocurrent recorded. In contrast, when the SNOM tip illuminates a region between two NRs (figures 4(d)–(f)), only the effect of one hot spot combined with a waveguide effect in one channel between the two NRs is present. This leads to a smaller amount of photocurrent measured in this region.

These effects combined with the effect of an increased area of the ZnO-NRs/organic layer interface, while increasing the length and diameter of ZnO-NRs, may also explain the observation that the average photocurrent increases when the length of ZnO-NRs increases (figure 3). Notice that an increased area of the ZnO-NRs/organic layer interface results in an increased effective area of the solar cell device. This leads to an increased number of separated/generated charges and thus to higher photocurrents. As a consequence, a higher power conversion efficiency of the photovoltaic device could be achieved. However, an increased effective area leads also to an increased surface saturation current which is detrimental for solar cell performance. Hence, an optimum effective area, i.e. an optimum ZnO-nanorod length should be found, that is a subject of a future study.

4. Conclusion

In conclusion, we investigated hybrid ZnO-NRs/C₆₀/ZnPc:C₆₀/MoO₃/Ag solar cells using SNOM. Simultaneous measurements of topography and near-field photocurrent were carried out. A high correlation

between the topography and photocurrent was found: the photocurrent produced on top of the ZnO-NRs is higher than that produced in other regions. It was also found that the average value of the local photocurrent increases as a function of the ZnO-NRs length. A finite element method simulation showed that this is mainly driven by the effect of electromagnetic hot spots and waveguide effect in the channels in between ZnO-NRs. The waveguide effect increases with increasing the ZnO-NRs length leading to the augmentation of the average value of the local photocurrent.

Our results lead to the interesting conclusion that this type of hybrid solar cells could benefit from placing nanoparticles at the bottom of the ZnO-NRs. They would then act as near-field generators channeling the light into the ZnPc:C₆₀ channel when illuminating from the ITO side, which is the standard configuration for such solar cells.

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