Plasmonic Metamaterials for Enhanced Organic Photovoltaics

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Abstract

In this paper the authors focus on two mechanisms to increase organic photovoltaic performance using plasmonic metamaterials: (1) light guiding into bloch mode resonances of a patterned metal surface and (2) near-field enhancements of the photo-physical properties of photo-responsive organic species. Our current work displays improvements in the photovoltaic performance, both in the device photo-physics and potentials for increases in off-angle photovoltaic response.

1. Introduction

Thin-film photovoltaics have become increasingly popular in the previous decade due to their lower manufacturing cost compared to bulk p-n junction cells. The flexibility that is inherent to plastic solar cells is also a large driver for their research. However, these devices suffer from much poorer photovoltaic conversion efficiency than their bulky solid-state counterparts. Therefore there is an urgent need to improve the efficiency of flexible and cheap organic thin film solar cells, but current research into alternative polymer materials has only yielded minor improvements over the last few years. Plasmonic metamaterials offer the opportunity to manipulate light with guided bloch plasmonic modes and to concentrate light with the use of resonant nanoparticles to create near-field effects on adjacent photo-responsive systems.

2. Experimental

The organic bulk heterojunction (org-BHJ) photovoltaic cell investigated in this paper is the routinely used poly-3-hexylthiophene blended with phenyl-C61-butyric acid methyl ester, commonly referred to as P3HT:PCBM. We use a 1:1 blend of the two species and spin cast films from dichlorobenzene. Film annealing is variable and several annealing procedures have been investigated. The film is sandwiched between an aluminium anode and a Baytron PH coated ITO film on glass. The Baytron PH is 50nm thick and provides an electron blocking layer at the ITO cathode. We are pursuing two separate yet complimentary methods to utilize plasmonic metamaterials in these cells to increase the overall photovoltaic response of the cells. In the first approach, we will discuss our results to intentionally pattern the back metallic anode in a way that promotes efficient coupling between incident radiation and horizontal bloch mode resonances. In the second approach, we will discuss our results in blending the organic PV active layer (BHJ) with plasmonic nanoparticles at varying concentrations.

3. Results

In the first approach, we have patterned the interface between an organic bulk heterojunction blend and the metallic device anode using a simple PDMS stamp with nanometer size features. This patterning is intended to produce propagating bloch modes that will resonate at the P3HT:PCBM / metal interface and better couple light into the active layer of the device. In these samples, the metal coated grating serves as a birefringent surface that scatters light throughout the cell more efficiently than a flat back electrode. Finite difference time domain (FDTD) studies are currently being preformed to optimize the back electrode features to couple to the back electrode through bloch mode resonances,

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which has recently been shown for Si:H devices by the Atwater group[1] that specific patterns designed using FDTD simulations will result in bloch-mode propagating plasmonic resonances to be excited by incident radiation. These modes run horizontal throughout the cell at the metal / dielectric interface and can result in higher off-angle external quantum efficiencies (EQEs). The same quantitative simulations are being performed on our organic bulk heterojunction materials to deduce superior patterning designs for back electrodes that will increase off-angle EQEs.

Fig. 1 (A) shows the resulting patterned P3HT:PCBM surface imaged via atomic force microscopy. This pattern matches the stamp features within 2% precision. Fig. 1 (B) is the I-V curve for a patterned device verses an unpatterned device. The efficiency increase from morphology changes alone is over 25%. The average film thickness of the patterened device is equal to the unpatterned device. These effects will be magnified for off angle illumination when using a pattern that can be excited through bloch mode resonances as in the previously reported Si:H devices[1].

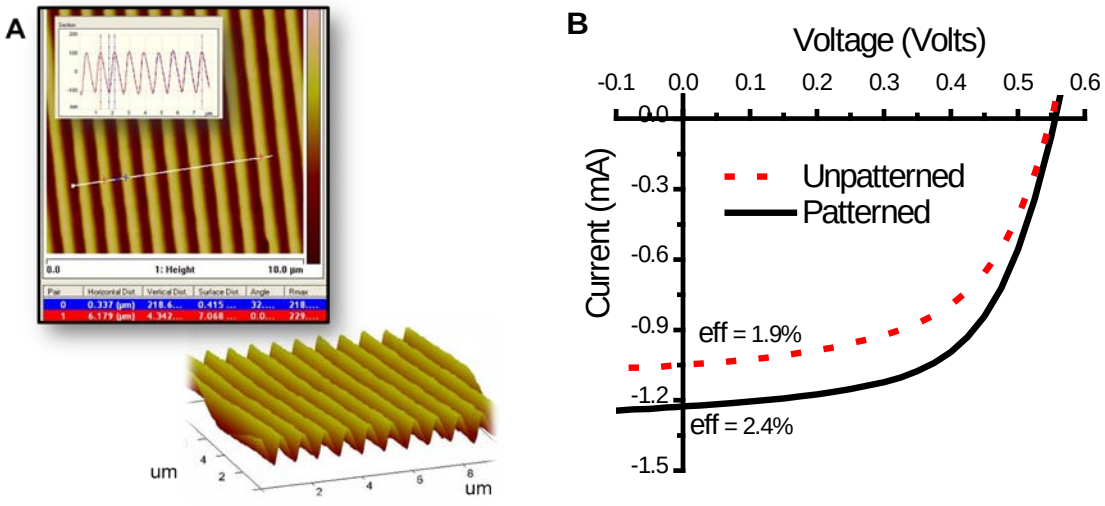

Fig. 1: A) AFM image of patterned P3HT:PCBM bulk heterojunction surface. B) I-V cures for patterned and unpatterned photovoltaic device using the same stamp used in 1A.

In the second approach, we have blended the organic photovoltaic bulk-heterojunction (P3HT:PCBM) with silver plasmonic nanoparticles. It is known throughout the literature that the strong plasmonic field concentrated at the surface of a metal nanoparticle during resonant excitation can have substantial effects on the photo-physical properties of the surrounding medium. This has been demonstrated for both enhancing and quenching molecular fluorescence[2] as well as other enhanced spectroscopies[3]. These effects result because the plasmonic particles serve as optical antennas to concentrate and focus the light to a much stronger intensity than is felt outside the field. In addition, increased scattering within the active layer should result from the inclusion of the plasmonic nanoparticles which act as dipole scatterers.

Fig. 2 (A) is the schematic device with plasmonic nanoparticles included in the org-BHJ layer. Fig. 2(B) is a transmission electron micrograph of the silver nanoparticles prior to inclusion in the P3HT:PCBM layer. Fig. 2 (C) shows the individual UV-Vis absorption spectra of the two species in the metamaterials:org-BHJ composite film. The blue spectrum is taken from silver nanoparticles (25nm diameter) suspended in dichlorobenzene. Once the particles are cast in the P3HT:PCBM film (spectrum shown in red), the higher index of the film (n≈1.6) will red-shift the plasmonic peak to coincide with the broad absorption band of the P3HT. Using the pump-probe technique photo-induced absorption, we observed the excited-state polaron population of the P3HT (positive free-carrier) in the film as a function of loaded nanoparticles. It was observed that by increasing the number of nanoparticles spin cast with the P3HT:PCBM film, the population of excited state polarons increased as well

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(Figure 2D). We are currently studying device performance of these films as a function of nanoparticle loading.

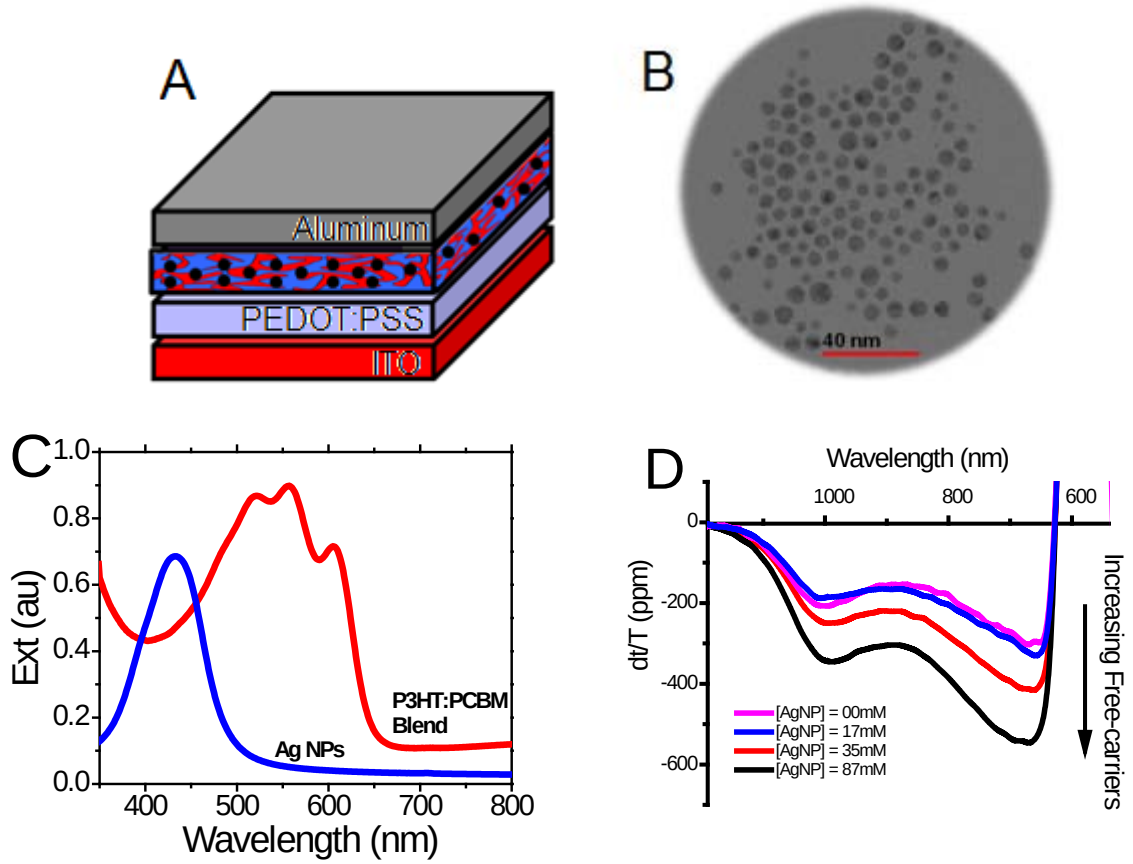

Fig. 1: A) Representative schematic of org-BHJ device with embedded plasmonic nanoparticles in the active layer. B) TEM image of silver nanoparticles prior to suspension in the P3HT:PCBM film. C) UV-Vis absorption spectra of plasmonic silver nanoparticles (blue) and P3HT:PCBM org-BHJ (red). D) Photo-induced absorption of positive polaron in P3HT:PCBM film as a function of nanoparticles spun with film.

4. Conclusion

In conclusion, we have demonstrated our approaches to integrating plasmonic metamaterials within organic photovoltaic films via two methods to improve inexpensive and flexible photovoltaic devices. This effort combines plasmonic metamaterials with contemporary design architectures for organic bulk heterojunctions to utilize sub-wavelength features to control and guide the incident radiation. We are able to utilize the light directing and concentrating properties of those materials to affect the light collection efficiencies of the PV device. Here we have demonstrated two approaches of this effort. The first showing increases in photovoltaic efficiency using imprinted metallic patterns and the second showing increases in excited state free carriers as a result of including plasmonic nanoparticles in the P3HT:PCBM film.

References

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