

Absorption and transport enhancement by Ag nanoparticle plasmonics for organic optoelectronics

Mei Xue,¹ Huajun Shen,¹ Jinfeng Zhu,¹ Seongku Kim,²
Lu Li,² Zhibin Yu,² Qibing Pei² and Kang L. Wang¹

¹Department of Electrical Engineering,

²Department of Materials Science and Engineering
University of California, Los Angeles, California 90095

mxue@ee.ucla.edu

Hussam Qasem, Abdullah A. Alzaben, Hani Enaya,
and Zaid S. Al Otaibi

Energy Research Institute,
King Abdulaziz City for Science and Technology (KACST)
Riyadh, Saudi Arabia

Abstract—The organic films such as P3HT/PCBM incorporating Ag metal nanoparticles are fabricated and experimentally characterized. Due to the excited surface plasma induced by Ag metal nanoparticles, the absorption of the active organic material layer is increased by around 30%. The broadened absorption spectrum to the 260-650nm wavelength range is also observed from our measurements because of the enhanced scattering cross section by Ag metal nanoparticles. Furthermore, by incorporating Ag nanoparticles into the active layer, the mobility have also been improved. Finite Difference Time Domain (FDTD) simulations confirm the increase in transmission of electromagnetic radiation at visible wavelength. The hopping model is proposed to explain the transport mechanism for the device operations. These observations suggest a variety of approaches for improving the performance of general organic optoelectronic devices.

Keywords—absorption; transport; surface plasma; metal nanoparticle; organic solar cell.

I. INTRODUCTION

Cost-effective photovoltaics has been extensively studied for alternative energy sources. Organic solar cells (OSCs) are of great current interest as they have a strong potential to reduce the cost of photovoltaic based on the high-throughput roll-to-roll process. [1-11] However, due to the short exciton diffusion length, OSCs with low absorption and mobility still have low efficiency comparing to silicon-based pn-junction solar cell. To increase the absorbance of very thin photoactive layers cells, surface plasmon resonances in metal has been used to take advantage of the large electromagnetic field enhancement near the metal surface and the strong dependence of the resonance wavelength on size, shape, and local dielectric environment of the metal nanostructures, which offer various tunability. [12-18] These devices rely on the local electric field enhancements caused by the surface plasmons of nanostructures.

In this letter, the organic films such as P3HT/PCBM incorporating Ag metal nanoparticles are fabricated. The absorption of the active organic material layer is theoretically and experimentally studied to show the increase of around 30%. Furthermore, the mobility has also been experimentally demonstrated to improve by incorporating Ag nanoparticles

into the active layer. Finite Difference Time Domain (FDTD) simulations using a cylindrical NPs model confirm the increase in transmission of electromagnetic radiation at wavelengths from 400nm to 900nm.

II. DEVICE FABRICATION

The fabrication of the active plasmonic solar cell started with electron-beam deposition of Ag metal on ITO with a deposition rate of 0.1 A/sec. It was followed by spin-coating a buffer layer of poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) using an aqueous solution (Baytron PVP Al 4083) onto Ag NPs/ITO substrate. Then an annealing process at 120 °C for 15 min was performed under air environment. The active material containing P3HT and PCBM with 1:1 weight ratio dissolved in 1,2-dichlorobenzene were spin-casted onto PEDOT:PSS to form a film of about 140 nm thick, followed by annealing process at 140 °C for 5 min in a nitrogen ambient glove box. Finally, the LiF/Al cathode was made using a thermal evaporation technique (Fig. 1(a)). The plasmonic testing structures were also fabricated using the same process except depositing the mixture layers of the active layer and silver nanoparticles with spin-coating a dichlorobenzene (DCB) solution of P3HT and PCBM mixed with Dodecanethiol functionalized 5-15 nm Ag nanoparticles hexane solution of different concentrations to produce an about 250nm thick hybrid bulk-heterojunction film.

III. RESULTS AND DISCUSSION

To verify the absorption enhancement of Ag nanoparticles, simulation of the plasmonic hybrid solar cell with Ag nanoparticles has been performed with a Finite-Difference Time-Domain (FDTD) method. The device structure and results are shown in Fig. 1. In our method, periodic boundary conditions and electromagnetic symmetries are assumed due to the hexagonal nanosphere periodicity, and perfectly matched layers are used as artificial absorbing layers to simulate optical open boundary conditions. We consider the general effect of metallic nanospheres on optical absorption in such structures and focus on the investigation at a 40nm thick active layer, by which is used under the trade-off of the bulk heterojunction versus optically thin film. Normalized optical absorption spectra of pristine and hybrid active layers are shown in Fig. 1

(b). The absorption spectra in hybrid active layers show an enhancement compared to the spectra of pristine active layers in the absorption bands of 360nm-650nm and 360nm-900nm for P3HT:PC60BM and PCPDTBT:PC70BM, respectively. The enhanced absorption peaks induced by the nanospheres are observed at about the wavelength 604nm for both blends. Particularly, the absorption enhancement near 604nm in the low band gap material, PCPDTBT:PC70BM, significantly compensates the low optical absorption of the pristine active layer in the longer wavelength range. The enhanced optical absorption is due to the near-field enhancement of absorption in bulk heterojunction blends.

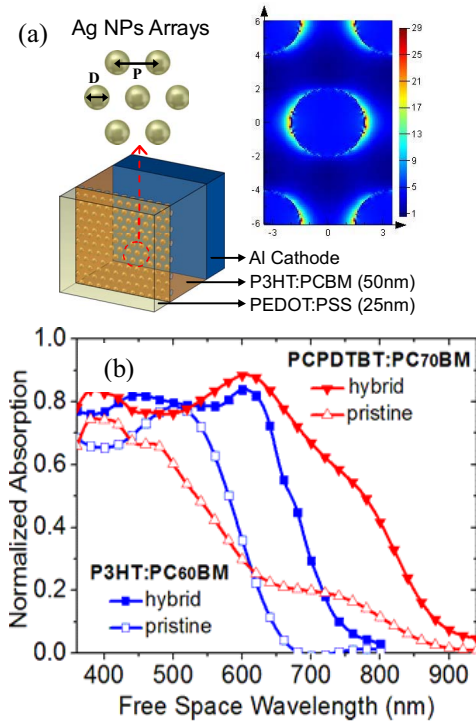


Figure 1. (a) Schematic structure of the simulated plasmonic OPV cell. D and P are the nanosphere diameter and period, respectively. (b) p-polarized incident absorption spectra of the pristine and hybrid active layers using P3HT:PC60BM and PCPDTBT:PC70BM, for D=15nm, and P=25nm.

The mobility of these devices has been studied using the Charge Extraction Linearly Increasing Voltage (Photo-CELIV) method. The standard pulse sequence and the schematic response of the Photo-CELIV technique are used in our measurements. The response of a dielectric upon application of a voltage ramp is a square-shaped current transient with the plateau value corresponding to the capacitive displacement current. If photo generated charge carriers are extracted from the dielectric, an additional extraction current is detected. From the time when the extraction current reaches its maximum value t_{max} , the mobility can be calculated as shown below. [19]

$$\mu = \frac{2d^2}{3At_{max}^2 \left[1 + 0.36 \frac{\Delta j}{j(0)} \right]} \text{ if } \Delta j \leq j(0)$$

where d is the thickness of the active layer, A is the voltage ramp slope, and t_{max} is the peak time. The recorded Photo-CELIV curves at various delay times are shown in Fig. 2. As the delay time increases, the maximum of the extraction current decreases and t_{max} slightly increases. The former is the effect of charge carrier recombination, and the latter indicates decreasing mobility. From the peak time for the different delay time, the mobility is calculated for the cells with different concentrations. The results are shown in Fig. 2 (b). Each data point was obtained from the average of at least five cells. Comparing to the standard devices without Ag nanoparticles, the devices with Ag nanoparticles show the significant improvement of the mobility. The highest mobility, in some cases, can reach about one order of magnitude higher than the standard devices. This is understandable from the hopping transport mechanism. Each Ag nanoparticles can be considered as the hopping center for the electron. Since they provide electrons with more transport paths, the mobility becomes larger.

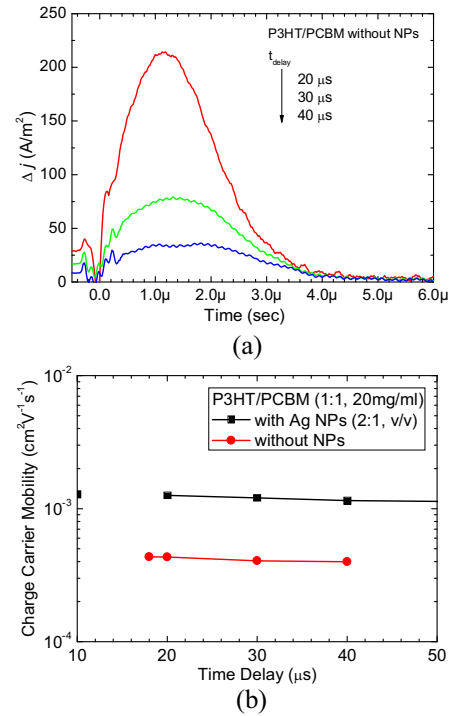


Figure 2. (a) CELIV measurement results of the reference sample with P3HT:PCBM (1:1) after subtracting the dark current. (b) Mobility comparison of P3HT/PCBM with and without Ag nanoparticles.

We have experimentally observed that the solar cell efficiency was increased by incorporating Ag nanoparticles as a 65 % increase of the photo-conversion efficiency as shown in Fig. 3. The IV characteristics of a solar simulator are measured. It is observed that comparing to the solar cell without Ag nanoparticles, the efficiency of the hybrid organic solar cell with Ag nanoparticles is obtained as a function of silver film thickness. The short-circuit current density with Ag-NPs of 5 nm thick obviously increases due to the enhancement of the photogeneration of excitons near the plasmonic resonance of

the Ag-NPs. The parameters such as J_{sc} [mA/cm²], V_{oc} [V], FF [%], and η [%] are 4.7 mA/cm², 0.59 V, 63.5 %, and 1.67 % for a regular solar cell, and 8.1 mA/cm², 0.58 V, 58.7%, and 2.75 % for a plasmonic hybrid organic solar cell, respectively.

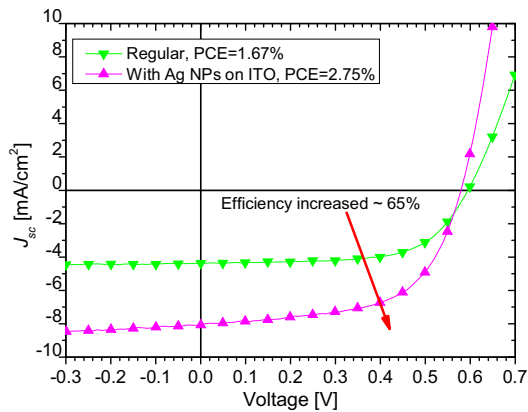


Figure 3. J_{sc} -V characteristics of an organic solar cell with and without Ag-NPs.

IV. CONCLUSION

Organic films P3HT/PCBM incorporating Ag metal nanoparticles have been studied for both absorption and transport characteristics. The absorption of the active organic material layer is increased by around 30% by FDTD simulation methods. Additionally the mobility has been experimentally demonstrated to be improved by incorporating Ag nanoparticles. These observations suggest a variety of approaches for improving the performance of general organic optoelectronic devices.

ACKNOWLEDGMENT

The authors would like to thank the partial support under the KACST-CAL Green Nanotechnology Center.

REFERENCES

- [1] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wedl, *Science* 258, 1474 (1992).
- [2] G. Yu, J. Gao, J. C. Hemmelen, F. Wudl, and A. J. Heeger, *Science* 270, 1789 (1995).
- [3] C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Funct. Mater.* 11, 15 (2001).
- [4] X. Yang, J. Loos, S. C. Veenstra, W. J. N. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels, and R. A. J. Janssen, *Nano Lett.* 5, 579 (2005).
- [5] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nat. Mater.* 4, 864 (2005).
- [6] K. Kim, J. Liu, M. A. G. Namboothiry, and D. L. Carroll, *Appl. Phys. Lett.* 90, 163511 (2007).
- [7] S.-S. Kim, S.-I. Na, J. Jo, G. Tae, and D.-Y. Kim, *Adv. Mater. Weinheim, Ger.* 19, 4410 (2007).
- [8] Sariciftci, N. S., Smilowitz, L., Heeger, A. J. & Wudl, F. Photoinduced electron transfer from a conducting polymer to buckminsterfullerene. *Science* 258, 1474–1476 (1992).
- [9] Yu, G., Gao, J., Hemmelen, J. C., Wudl, F. & Heeger, A. J. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor–acceptor heterojunctions. *Science* 270, 1789–1791 (1995).
- [10] Halls, J. J. et al. Efficient photodiodes from interpenetrating polymer networks. *Nature* 376, 498–500 (1995).
- [11] Kim, J. et al. Efficient tandem polymer solar cells fabricated by all-solution processing. *Science* 317, 222–225 (2007).
- [12] J. D. Driskell, R. J. Lipert, and M. D. Porter, *J. Phys. Chem.* 110, 17444 (2006).
- [13] D. W. Pohl, *Near-Field Optics and Surface Plasmon Polaritons* Springer, Heidelberg, (2001).
- [14] Y.-C. Nah, S.-S. Kim, J.-H. Park, and D.-Y. Kim, *Electrochem. Solid-State Lett.* 10, J12 (2007).
- [15] Y.-C. Nah, S.-S. Kim, J.-H. Park, H.-J. Park, J. Jo, and D.-Y. Kim, *Electrochem. Commun.* 9, 1542 (2007).
- [16] H.-J. Park, D. Vak, Y.-Y. Noh, B. Lim, and D.-Y. Kim, *Appl. Phys. Lett.* 90, 161107 (2007).
- [17] B. P. Rand, P. Peumans, and S. R. Forrest, *J. Appl. Phys.* 96, 7519 (2004).
- [18] S. Uemura, M. Yoshida, T. Kodzasa, K. Yase, and T. Kamata, *Synth. Met.* 137, 1443 (2003).
- [19] Mayer, A. C.; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D. *Mater. Today* 2007, 10, 28–33.