Supporting Information

Nano-bio Hybrids of Plasmonic Metal/Photosynthetic Protein for Broad-band Light Absorption Enhancement in Organic Solar Cells

Kai Yao, Huifeng Jiao, Yun-Xiang Xu, Qiqi He, Fan Li, Xiaofeng Wang

METHODS

Materials. PIDTT-DFBT^[S1], PBDT-DTNT^[S2] and C_{60} -SAM^[S3] were synthesized as previous reports, and PTB7-Th and PC₇₁BM were purchased from 1-material Chemscitech and used as received.

Preparation of nanoparticles. Ag nanoprism were synthesized according to modified Kelly's method^[S4]. In a typical experiment, silver seeds were produced by combining aqueous solutions of sodium citrate (2.5 mM, 20 mL), poly(sodium styrenesulphonate) (PSSS; 0.5 mg/mL, 1 mL) and freshly prepared NaBH₄ (10 mM, 1.2 mL) followed by addition of aqueous AgNO₃ (0.5 mM, 20mL) at a rate of 2 mL/min while stirring continuously for 20 min after addition of AgNO₃. The solution was then left to sit overnight before use. The nanoprisms were produced by combining various quantities of seed solution with 33.3 mL distilled water and aqueous ascorbic acid (10 mM, 0.5 mL), followed by addition of aqueous AgNO₃ (0.5 mM, 20 mL) at a rate of 1 mL/min. Sodium citrate (25 mM, 3.3 mL) was added after synthesis to stabilize the nanoparticles. The synthesis was complete after the 20 minutes required for addition of the AgNO₃ during which time the solution color changed due to nanoprism growth. Silver nanoparticles with extinction peaks ranging from ~ 380 nm to ~ 650 nm in water were made using this method. Specifically, nanoprism Ag-NPs 530 with extinction peaks at 530 nm was used and 16-Mercaptohexadecanoic acid (MHDA) (1 mM) was added to the stripped Ag NPs samples. The sizes of the Ag-NPs nanoprisms were characterized by a FEI Tecnai G2 F20 transmission electron microscopy (TEM) operated at an acceleration voltage of 200 kV.

Preparation of LHCII and hybrids. Fresh spinach leaves with good turgor and dark green color were used. LHCII was isolated according to the protocol described previously^[S5]. And the chlorophyll concentration and chlorophyll a/b ratio (~ 1.3) were measured according to the

procedure described by Arnon^[S6]. For the present experiments this stock solution was diluted into various concentrations and 2% polyvinyl alcohol (PVA) was added. Finally, different concentrations of LHCII and Ag-530 solution were mixing together for using in our work.

Device Fabrication and Characterization:

For normal ITO-based control devices: ITO-coated (15 Ω /sq) glass substrates were cleaned sequentially with a detergent, DI-water, acetone, and isopropanol. Prior to the fabrication of the organic layers, the ITO surface was treated with UV-Ozone. As for the devices with an inverted structure, the prepared ZnO sol-gel was spin-coated on the pre-cleaned ITO-coated glass substrate at 4000 rpm. The ZnO films were annealed at 200 °C for 1 h in the air. The C₆₀-SAM and APS were deposited on the ZnO surface using a two-step spin process, while the Ag-530, LHCII and Ag-530/LHCII hybrids solutions in various concentrations were spin-casted on the ZnO surface modified with 3-aminopropyltriethoxysilane (APS) at a spin rate of 4000 rpm for 1 min. Afterwards, PIDTT–DFBT:PC₇₁BM (20 mg/mL, 1:3.5, w/w) in a mixture of 1,2-dicholobenzene (o-DCB) and 1-chloronaphthalene (v/v, 97:3) solution was spin-coated on the ZnO layer with various interlayer at 1000 rpm inside a nitrogen glove box (O_2 and H_2O concentration <1ppm), and subsequently dried in a vacuum chamber under nitrogen atmosphere to obtain a film thickness of approximately 85 nm. PBDT-DTNT:PC₇₁BM at a weight ratio of 1:1.5 (1:1.5 w/w, 25 mg/mL) in o-DCB was spin-coated at 1200 rpm for 2 min on different surface-modified ZnO layer layers. The PTB7-Th:PC71BM (1:1.5 w/w, 25 mg/mL) active layer was prepared by spincoating a mixed solvent of chlorobenzene/1,8-diiodoctane (97:3 v/v) solution on different surface-modified ZnO layer layers. Finally, 8 nm MoO₃ and 100 nm Ag were deposited sequentially under high vacuum by thermal evaporation onto the active layer through shadow masks to define a device area of 9.60 mm².

A Keithley 2400 source meter unit was used to record J-V characteristics in this study. A 300 W xenon arc solar simulator equipped with an AM 1.5G filter was used to simulate a light intensity of 100 mW cm⁻². The illumination intensity of the light source was accurately calibrated

employing a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory (NREL). The EQE spectra performed here were obtained from an IPCE setup consisting of a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, a chopper with a frequency of 100Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration. The calculated J_{SC} values obtained by integrating the EQE spectrum under the AM 1.5G illumination condition agreed well with the measured J_{sc} value from J-V characteristics and the differences were within 3%.

Optical Simulations:

In the TMM simulation, we assumed planar interfaces and isotropy for all the films. The optical nature of each material was represented by their complex refractive index ($\tilde{n} = n + ik$) acquired by a variable angle spectroscopic ellipsometer (VASE) from J.A. Woollam Co. The simulation considered that the substrate was much thicker than the wavelengths of the simulated light. As a result, the interference is incoherent within the substrate.

Simulation Details:

In the simulations, a commercial grade FDTD simulator package, Lumerical FDTD Solutions 8.7.4. We have meshed the simulation region $(1 \ \mu m \times 1 \ \mu m)$ using staircase mesh in order to separate the absorption due to metal nanoparticles using a refractive index filter. We positioned particles in the simulation region and change their orientations using random numbers from a continuous uniform distribution. The boundary conditions after this randomization are chosen to be periodic. The refractive index filter for absorption works by zeroing the absorption at points where the index of refraction is equal to Ag at that wavelength. We used the methods described here (http://docs.lumerical.com/en/fdtd/solar_plasmonic_definitions.html) to calculate J_{sc} from absorption.

Dependence of the J_{ph} on the V_{eff}

 $J_{\rm ph}$ was calculated according $J_{\rm ph} = J_{\rm L} - J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are the current density under illumination and in the dark, respectively. $V_{\rm eff}$ was determined by $V_{\rm eff} = V_{\rm o} - V_{\rm a}$, where $V_{\rm o}$ is the voltage at which $J_{\rm ph} = 0$ and $V_{\rm a}$ is the applied bias voltage. At a sufficiently high value of $V_{\rm eff}$, we can obtain the saturated current $J_{\rm ph}$. $G_{\rm max}$ could be estimated according to the formula $J_{\rm sat} = qG_{\rm max}L$, where q is the electronic charge and L is the thickness of the active layer (~ 85 nm).

SCLC Mobility Measurement. Space charge limited currents have been tested in electron only devices with a configuration of ITO/Al/interlayer/polymer:PCBM/Ca/Al. The devices were prepared following the same procedure described in the experimental section for photovoltaic devices, except that of the metal electrode. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as

$$J = \frac{9\varepsilon_{\rm r}\varepsilon_0\mu_0V^2}{8L^3}\exp(\beta\sqrt{\frac{V}{L}})$$

where *J* is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, *V* is the effective voltage, and *L* is the thickness of the active layer.

Table S1 Surface roughness of AFM images for ZnO film with different interfacial materials.

Film Type	Bare ZnO	C ₆₀ -SAM	Ag-530*	LHCII*	Ag-530/LHCII*
RMS Roughness (nm)	1.32	1.68	4.97	3.06	2.67

*The ZnO layers are modified with APS.

Table S2 The relative thickness of pure LHCII layer, Ag NPs layer and blending layers with different Ag NPs concentration (0.5, 1.0 and 2.0 mg/mL) on ZnO/APS surface.

Lover	Relative thickness ^a (nm)				
Layer	1	2	3	Average	
LHCII (0.05 mg/mL)	6.7	4.9	7.5	6.4	
LHCII (0.1 mg/mL)	10.1	8.4	11.8	10.1	
LHCII (0.2 mg/mL)	18.9	22.2	16.8	19.3	
Ag-530 (1 mg/mL)	12.9	9.6	15.2	12.6	
Ag-530 (0.5 mg/mL)/ LHCII (0.1 mg/mL)	14.1	18.3	16.8	16.4	
Ag-530 (1 mg/mL)/ LHCII (0.1 mg/mL)	21.1	23.3	18.2	20.8	
Ag-530 (2 mg/mL)/ LHCII (0.1 mg/mL)	31.2	34.0	28.9	31.3	

^aThe relative thickness of each sample was measured with Atomic Force Microscope (AFM) and each sample was measured independently 3 times in different area to obtain an average thickness.

System	Туре	η (%) (Average) ^[a]	Enhancement Factors (%)	Reference
PBDTTT-C-T: PC ₇₁ BM	Nanograting Electrode + Au NPs in BHJ	8.79 (7.59)	15.8	S 7
PTB7:PC ₇₁ BM	Ag@SiO ₂ on PEDOT:PSS	8.49 (7.26)	16.9	S8
PTB7-Th:PC71BM	Au@Ag@SiO ₂ on PEDOT:PSS	10.42 (9.13)	14.1	S9
PTB7:PC ₇₁ BM	Au:BCNT in BHJ	9.75 (8.12)	20.1	S10
PTB7-Th:PC71BM	Aperiodic ZnO nanostructures	8.34 (9.94)	19.2	S11
PIDTT- DFBT:PC ₇₁ BM	Ag-530/LHCII on ZnO	7.40 (8.94)	20.8	Our work
PTB7-Th:PC ₇₁ BM	Ag-530/LHCII on ZnO	9.03 (10.57)	17.1	Our work

Table S3 Comparison of our work with other high performance PSCs using light.

^[a]Reference PCE values in the brackets



Fig. S1 J-V characteristics of devices architecture ITO/ZnO/APS/LHCII/PIDTT-DFBT:PC₇₁BM/MoO₃/Ag as a function of LHCII thickness. The concentrations of LHCII solutions are 0.05, 0.1 and 0.2 mg/mL for the fabrication of 6, 10 and 20 nm, respectively. The corresponding series resistance of the devices is presented.



Fig. S2 UV-vis spectra of a series of as-prepared Ag nanoprisms with various extinction peaks.



Fig. S3 TEM images of silver nanoprisms Ag-530 from a typical sample.



Fig. S4 SEM image of the nano-bio hybrids Ag-530/LHCII on the surface of ZnO/APS film.



Fig. S5 The chemical structure of the SAM (C₆₀-COOH) and AFM height images $(5.0 \times 5.0 \ \mu\text{m}^2)$ of the ZnO surface with SAM modification and incorporation of the nano-bio hybrids.



Fig. S6 Optimization of the hybridizing condition for the best performance in the PIDTT-DFBT/PC₇₁BM device: (A) *J-V* characteristics of reference devices and the plasmonic devices; (B) *J-V* characteristics of hybrid devices with different concentration of silver nanoprism.



Fig. S7 Current density–voltage (*J*–*V*) curves of the PIDTT-DFBT/PC₇₁BM device without and with various interlayers in optimal performance. The incorporation of Ag-530/LHCII raise the maximum PCE of 9.39% in PIDTT-DFBT/PC₇₁BM device.



Fig. S8 UV-Vis absorption spectrum of activelayer PIDTT-DFBT:PC₇₁BM on the substrates with or without modified layer.



Fig. S9 Optical enhancement study of PIDTT-DFBT/PC₇₁BM devices with LHCII or Ag-530/LHCII layer: Left: the extracted absorption enhancement factors, $\Delta A/A_{ref}$ ($\Delta A = A_{plasmonic} - A_{ref}$); Right: EQE enhancement factors, $\Delta EQE/EQE_{ref}$ ($\Delta EQE = EQE_{plasmonic} - EQE_{ref}$) compared with control device.



Fig. S10 Dark *J-V* characteristics of inverted PIDTT-DFBT/PC₇₁BM devices with different interfacial materials on ZnO layer.



Fig. S11 The J-V characteristics of electron only devices in different structures. The bias is corrected for built-in Voltage V_{Bi} , arising from difference in the work function of the contacts, and the voltage drop due to substrate series resistance, such that $V = V_{\text{APPL}} - V_{\text{RS}} - V_{\text{Bi}}$. The solid lines represent the fitting curves. Estimated by the SCLC model, the electron mobilities showed small variation.



Fig. S12 UPS spectra evolution at the low kinetic energy region (secondary electron cutoff) for work functions of different interfacial layers.



Fig. S13 Calculated photocurrent (J_{ph}) of the devices assuming that various interfacial materials SAM (5 nm) and Ag NPs–LHCII complex (20 nm) only played as optical spacer.



Fig. S14 Photoluminescence spectra of thin films of LHCII and nano-bio hybrids on a quartz plate, excited at 530 nm. In the figure A, the peak separation data of bilayer films for LHCII and PIDTT-DFBT are presented in gray and pink curves, respectively.



Fig. S15 EQE spectra of the control devices and device with hybrid interlayer for PBDT-DTNT: $PC_{71}BM$ (B) and PTB7-Th: $PC_{71}BM$ (C) systems.

Supporting Reference

[S1] Y. X. Xu, C. C. Chueh, H. L. Yip, F. Z. Ding, Y. X. Li, C. Z. Li, X. S. Li, W. C. Chen and A. K. Y. Jen, Adv. Mater., 2012, 24, 6356–6361.

[S2] M. Wang, X. W. Hu, P. Liu, W. Li, X. Gong, F. Huang and Y. Cao, J. Am. Chem. Soc., 2011, 133,9638–9641.

[S3] S. K. Hau, Y.-J. Cheng, H.-L. Yip, Y. Zhang, H. Ma, A. K. Y. Jen, ACS Appl. Mater. Interfaces, 2010, 2, 1892.

[S4]D. Aherne, D. M. Ledwith, M. Gara and J. M. Kelly, Adv. Funct. Mater. 2008, 18, 2005.

[S5] Y. Yang, R. Jankowiak, C. Lin, K. Pawlak, M. Reus, A. R. Holzwarth and J. Li, *Phys. Chem. Chem. Phys.* 2014, *16*, 20856.

[S6] D. I. Arnon, Plant Physiol. 1949, 24, 1-15.

[S7] X. Li, W. C. Choy, L. Huo, F. Xie, W. E. Sha, B. Ding, X. Guo, Y. Li, J. Hou, J. You and Y. Yang, *Adv. Mater.* **2012**, *24*, 3046.

[S8] H. Choi, J. P. Lee, S. J. Ko, J. W. Jung, H. Park, S. Yoo, O. Park, J. R. Jeong, S. Park and J. Y. Kim, *Nano Lett.* **2013**, *13*, 2204.

[S9] S. Liu, R. Jiang, P. You, X. Zhu, J. Wang and F. Yan. Energy Environ. Sci. 2016, 9, 898.

[S10] J. M. Lee, J. Lim, N. Lee, H. I. Park, K. E. Lee, T. Jeon, S. A. Nam, J. Kim, J. Shin and S. O. Kim, *Adv. Mater.* **2015**, *27*, 1519.

[S11] J. D. Chen, C. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. Li and J. X. Tang, *Adv. Mater.*, **2015**, *27*, 1035.