Electronic Supplementary Information

Fabrication of tunable aluminum nanodisk arrays via a self-assembly nanoparticles template method and their application in performance enhancement in organic photovoltaics

Zhiqiang Liang[a‡], Wenkai Liang[a‡], Weijing Shao[a], Jing Huang[a], Tianfu Guan[a], Peng Wen[a], Guozhong Cao[b]* and Lin Jiang[a]*

[a] Institute of Functional Nano & Soft Materials Laboratory (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, Jiangsu 215123, China.

[b] Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120, USA.

*Guozhong Cao, E-mail address: gzcao@u.washington.edu
*Lin Jiang, E-mail address: ljiang@suda.edu.cn
‡ Zhiqiang Liang and ‡ Wenkai Liang contributed equally to this work.

1. Experimental Details of the Fabrication of Al Nanodisk Arrays:

To fabricate the aluminum (Al) nanodisk arrays on ITO/TiO_2 substrate for performance enhancement in bulk heterojunction (BHJ) organic photovoltaics (OPVs), sequential nanofabrication processes of PMMA pattern, Al deposition and subsequent lift-off process were applied. The detailed fabrication procedure and experimental parameters are presented as following:

1.1 Preparation of PMMA Pattern:

Firstly, Al nanodisk arrays preparation started with the fabrication of PMMA pattern, which with the nanostructure of hole arrays. To obtain PMMA pattern with designated holes structure, Au NPs with diameters of around 90 ~ 120 nm were synthesized and assembled on TiO_2 substrate first. Au NPs were prepared using procedures described previously.[1] Prior to the assembly of Au NPs, ITO/TiO_2 substrates were performed a surface modification utilizing an oxygen (O_2) plasmon treatment and subsequently immersing the ITO/TiO_2 substrates into ethanol solution of MPTES (6 Vol %) and aqueous solution of H_2O_2 (30 Vol %) for 12 hours and 3 hours, respectively, and finally rinsed in DI water. After that, Au NPs were assembled onto TiO_2 surface by immersing the ITO/TiO_2 substrates into Au NPs aqueous solution and holding for 8 hours (Fig. 1a). Then the obtained ITO/TiO_2/Au NPs substrates were rinsed using DI water and dried under N_2 gas flow prior to coat PMMA layer.

Secondly, for fabricating a replica from the assembled Au NPs, an around 130 nm thick PMMA layer was spin-coated onto Au NPs (Fig. 1b). The toluene solution of PMMA (Mw = 99 K) was prepared by dissolving 0.4 g PMMA in toluene (10 ml) under ultrasonic agitation. Then the PMMA solution was dropped onto ITO/TiO_2/Au NPs substrates and spin-coated at 3000 rpm for 30 s and baked at 70 °C for 5 min immediately in air on a hot-plate to drive away residual solvent. After that, the PMMA layer was partly etched by O_2 plasmon at 200 Watts power for 4 min for etching out around half the thickness of PMMA layer so that to expose the top of Au NPs (Fig. 1c).

Thirdly, after the removal of Au NPs by immersing the samples into a KI solution for a quick rinse, PMMA pattern with hole arrays structure was achieved on TiO_2 surface (ITO/TiO_2/PMMA pattern) (Fig.e 1d).

1.2 Al Deposition and Lift-off:

A 30 nm thick Al layer was deposited on the ITO/TiO_2/PMMA pattern using a vacuum thermal evaporator under a vacuum of 8×10^{-5} Pa (Fig. 1e). Successively, a lift-off process was performed by immersing the samples in N-Methyl pyrrolidone (NMP) solution at 60 °C for 30 min to remove the residual PMMA and the Al layer on the top of PMMA pattern. It should be noted that, in order to favor the lift-off process, the thickness of Al layer should be controlled. Finally, Al nanodisk arrays with an average disk diameters of ~ 130 nm were obtained (Fig. 1f). After that, ITO/TiO_2 substrates with or without Al nanodisk arrays were subsequently transferred to an inert N2-filled glove-box for organic solar cells fabrication.

2. FDTD calculation:

The finite-difference time-domain (FDTD) simulations were performed using a commercial software (FDTD solutions 8.15, Lumerical solutions, Inc., Vancouver, Canada). The Al nanodisk was placed on the top of 35 nm TiO_2 substrate and in a surrounding of air and active layer, respectively. According to the SEM and AFM measurements results, the shape of Al disk was modeled as an inverted truncated cone with top and bottom diameters of 130 nm and 50 nm, respectively. The height was set at 30 nm, as obtained from the AFM height profile. In addition, the outermost surface of the Al nanodisk model was assumed to be covered with a 3 nm Al_2O_3 shell. To get accurate results, override mesh regions were used for each part of the modeled structure. Specifically, a mesh size as small as 0.8 nm was used at the interface region between Al_2O_3 and TiO_2 and a mesh size of 3 nm was used in other regions for simulation. A total-field scattered-field plane wave source was selected to estimate the interaction between propagating plane waves and the Al nanodisk arrays. The optical constants of Al_2O_3 tabulated in Ref. 2 were used. The incident wavelengths were set from 400 nm to 850 nm with a step of 2.25 nm. Polarization was selected to parallel to the interface.

3. Figures and Their Captions

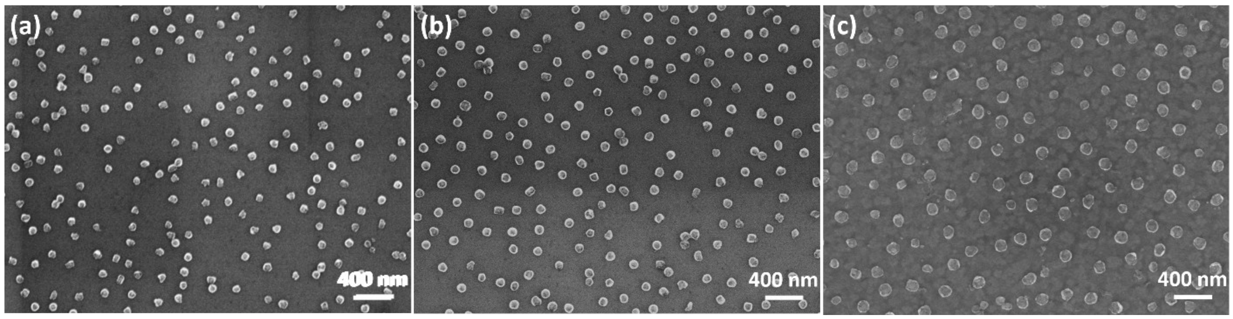

Fig. S1. SEM images of Al nanodisk arrays with different diameters. a) ~ 90nm, b) ~ 100 nm and c) 130 nm.

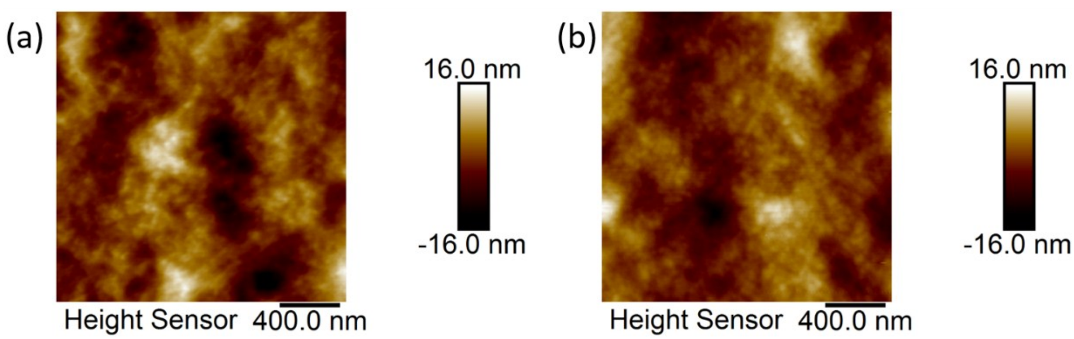

Fig. S2. AFM topographic images of P3HT:$PC_{61}BM$ active layer deposited on (a) pristine TiO_2 dense film and (b) TiO_2/Al nanodisk arrays.

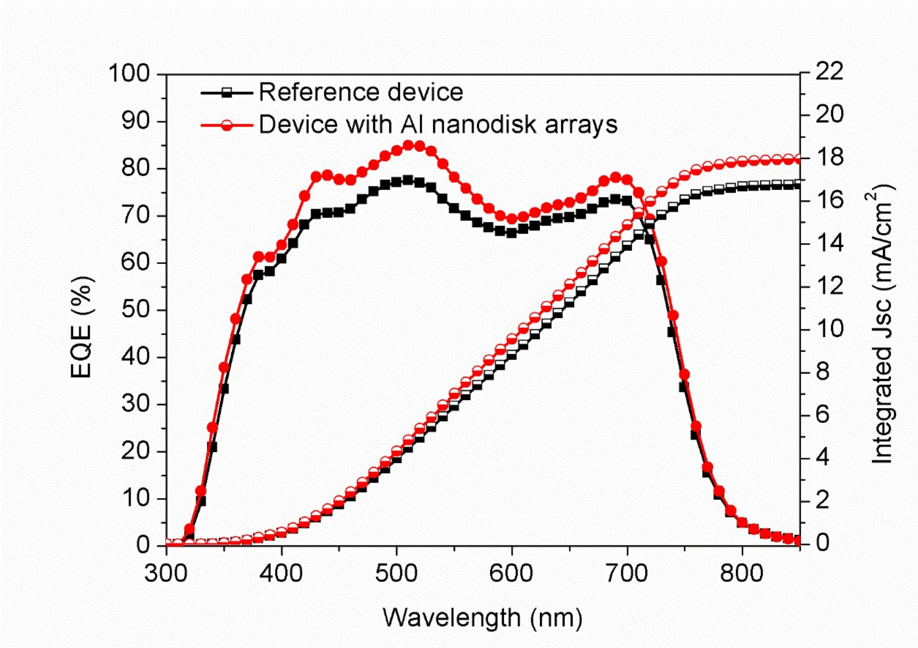

Fig. S3. EQE spectra of the representative reference device and Al nanodisk arrays enhanced device with PTB7:$PC_{71}BM$ active layer.

References for Supplementary Information:

(1) Ruan, Q.; Shao, L.; Shu, Y.; Wang, J.; Wu, H. Growth of Monodisperse Gold Nanospheres with Diameters from 20 nm to 220 nm and Their Core/Satellite Nanostructures. *Advanced Optical Materials* **2014,** *2* (1), 65-73.

(2) Palik, E. D. Handbook of Optical Constants. *AcademicPress: San Diego, CA* **1998**.