

## Supporting Information

# Efficient Light Trapping in Inverted Polymer Solar Cells by Randomly Nanostructured Electrode Using Monodispersed Polymer Nanoparticles

Dong Jin Kang<sup>1,3</sup>, Hyunbum Kang<sup>1,3</sup>, Changsoon Cho<sup>2,3</sup>, Ki-Hyun Kim<sup>1,3</sup>, Seonju Jeong<sup>2,3</sup>, Jung-Yong Lee<sup>2,3,\*</sup>, Bumjoon J. Kim<sup>1,3,\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, <sup>2</sup>Graduate School of Energy, Environment, Water, and Sustainability (EEWS), <sup>3</sup>KI for the NanoCentury, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

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\*E-mail: [bumjoonkim@kaist.ac.kr](mailto:bumjoonkim@kaist.ac.kr), [jungyong.lee@kaist.ac.kr](mailto:jungyong.lee@kaist.ac.kr)

## EXPERIMENT

### Materials

60 nm polystyrene nanoparticles (PS NPs) were synthesized by emulsion polymerization and commercial PEDOT:PSS in water (Baytron 4083) was used as anode buffer layer (ABL). Commercial P3HT (BASF P200) was used as an electron donor, and OXCBA or PCBM was used as an electron acceptor.

### Synthesis of PS colloid

PS NPs were synthesized by emulsion polymerization. Styrene monomer was purified with an aluminum oxide column. The other organic reagents were used without further purification, including poly(vinylpyrrolidone) ( $M_w = 55,000$  g/mol), and 2,2-azobis(isobutyronitrile) (AIBN). PVP and AIBN were dissolved in deionized water in a 500 mL two-neck flask, and the styrene was added to the solution. The reaction temperature was gradually increased to 70 °C and kept at this temperature for 24 h before the reactant was finally allowed to cool to room temperature. As-synthesized PS NPs were filtered and washed to remove the residual styrene and PVP with water and methanol. The sample was dried in a vacuum oven at 50 °C for 12 h. The size and size distribution of PS NPs were obtained from a Hitachi S-4800 scanning electron microscope (SEM) as shown in **Figure S1**.

### Devices Fabrication and Measurement

To investigate the light trapping effect of nanostructured Ag electrode on inverted polymer solar cells (PSCs), BHJ photovoltaic cells using an ITO/ZnO/P3HT:OXCBA/PS NP-PEDOT:PSS/Ag structure were fabricated; P3HT was used as an electron donor, and OXCBA was used as an electron acceptors. ITO-coated glass substrates were subjected to ultra-sonication in acetone and 2% Helmanex soap in water, followed by extensive rinsing

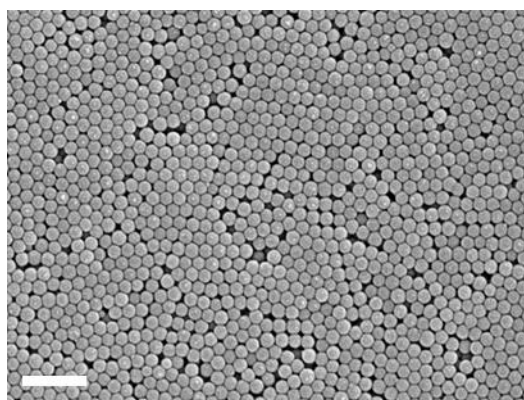
with deionized water and ultrasonication in deionized water and then in isopropyl alcohol; the substrates were finally dried for several hours in an oven at 80 °C. The ZnO was prepared using a sol-gel procedure, dissolving zinc acetate dihydrate ( $\text{Zn}(\text{O}_2\text{CCH}_3)_2 \cdot (\text{H}_2\text{O})_2$ , 99.9%, 1 g) and ethanolamine ( $\text{HOCH}_2\text{CH}_2\text{NH}_2$ , 99.5%, 0.28 g) in anhydrous 2-methoxy ethanol ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ , > 99.8%, 10 mL) under vigorous stirring for more than 24 hrs to allow the hydrolysis reaction. ZnO thin films with a thickness of ~40 nm were prepared by spin-coating the sol-gel precursor solution at 3000 rpm on top of the ITO substrate. The films were heated at 200 °C for 1 hr in air. After deposition of the ZnO layer, all subsequent procedures were performed in a glove box under a  $\text{N}_2$  atmosphere. Solutions of P3HT and OXCBA were prepared in o-dichlorobenzene and stirred at 100 °C overnight to ensure complete dissolution. Immediately prior to solution deposition, the solutions were passed through a 0.2 and 0.45- $\mu\text{m}$  polytetrafluoroethylene syringe filter. The blend solution was stirred at room temperature for 1 h and then spun-cast onto the ITO/ZnO substrates at 900 rpm. P3HT/acceptor film was dried and the thickness of films was approximately 100 nm. PEDOT:PSS (VAITRON AI 4083) and PS NP-PEDOT:PSS ink were then spin-cast at 4000 rpm on top of the aforementioned layer using X-triton 100 (1~1.5 wt%) as a processing additive to form a smooth layer with a thickness of ~50 nm<sup>[1]</sup> and then annealed at 120 °C in the glove box. Finally, to complete the devices, the top electrode, a ~100 nm Ag film, was thermally evaporated under high vacuum (less than  $10^{-6}$  Torr).

Field emission SEM (Hitachi S-4800), atomic force microscopy (AFM, Veeco, Nanoman) and transmission electron microscopy (TEM, JEOL 2000FX) studies were performed to observe the morphology of the ABL samples. The cross-sectional TEM samples were prepared by focused ion beam (FIB) using Quanta 3D FEG. The photovoltaic performances were characterized using a solar simulator (Newport Oriel Solar Simulators) with an air-mass (AM) 1.5 G filters. The intensity of the solar simulator was calibrated using

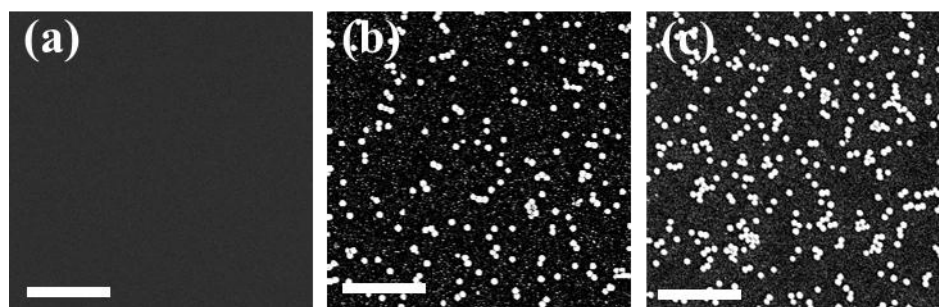
an AIST-certified silicon photodiode. Current-voltage behavior was measured using a Keithly 2400 SMU. The active area of the fabricated devices was 0.09 cm<sup>2</sup>.

### Light Scattering Ratio Measurement

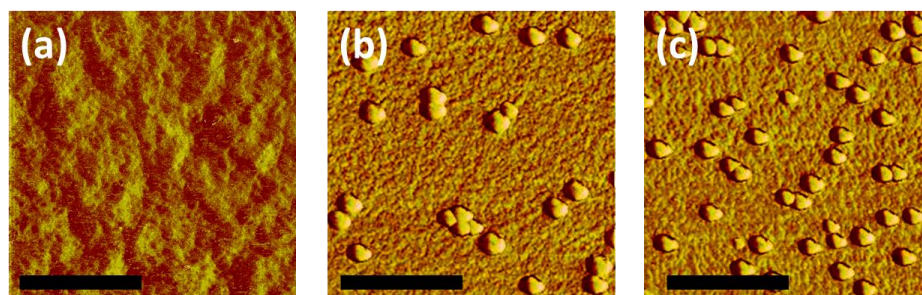
To investigate quantitative light scattering effect, reflectances of the flat ( $\phi_{\text{NP}} = 0$ ) and nanostructured ( $\phi_{\text{NP}} = 0.31$ ) devices were measured with and without an integrating sphere as shown in **Figure S4**. While total reflectance including the diffuse reflectance is taken into account with an integrating sphere, only the specular reflectance is without an integrating sphere. Conceivably, since the nanostructured back electrodes scattered incident light the reflectances with and without an integrating sphere showed large difference in the nanostructured ( $\phi_{\text{NP}} = 0.31$ ) device while they were almost same in the flat ( $\phi_{\text{NP}} = 0$ ) device over the entire wavelength range (400~700 nm). And the difference of the reflectance for the nanostructured device peaks at around 420 nm, where the EQE enhancement became stronger as shown in the inset of Figure 4(a), possibly due to surface plasmon resonance effect by the nanostructured Ag electrode.<sup>[2]</sup>



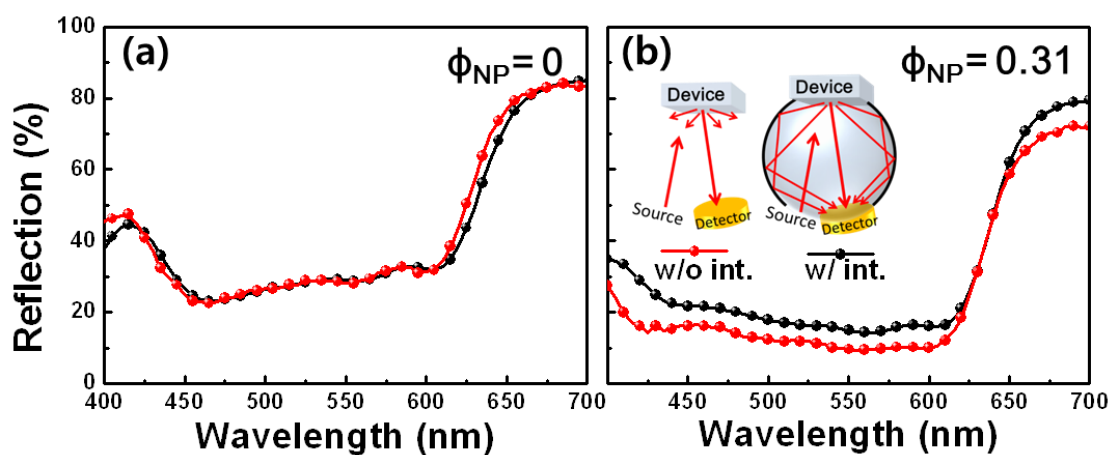
**Figure S1.** Monodispersed 60nm PS NPs synthesized by emulsion polymerization. The scale bar is 300 nm.



**Figure S2.** SEM images show the surface morphologies of the PS NP-PEDOT:PSS ABL with different  $\phi_{\text{NP}}$  values of (a)  $\phi_{\text{NP}}=0$ , (b) 0.24, and (c) 0.42. The presence of PS NPs is clearly evident only in Figures (b) and (c); The scale bar is 1  $\mu\text{m}$ .



**Figure S3.** AFM images show the surface morphologies of the PS NP-PEDOT:PSS ABL with different  $\phi_{\text{NP}}$  values of (a)  $\phi_{\text{NP}}=0$ , (b) 0.24, and (c) 0.42. The scale bar is 300 nm.



**Figure S4.** Measured reflection spectra with and without an integrating sphere at the  $\phi_{NP}$  values of (a)  $\phi_{NP}=0$ , and (b)  $\phi_{NP}=0.31$ .

**Table S1.** Film thickness and surface roughness of PS NP-PEDOT:PSS films at optimized device conditions.

$\phi_{NP}$	Thickness (nm)	Surface roughness (RMS, nm)
0	47.8	0.7
0.24	59.1	12.4
0.31	60.1	12.0
0.42	60.9	10.2

## References

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- [2] Li, X. H.; Sha, W. E. I.; Choy, W. C. H.; Fung, D. D. S.; Xie, F. X. *J. Phys. Chem. C* **2012**, *116*, 7200.