Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2014

# **Supporting Information**

### Enhanced efficiency of solution-processed small-molecule solar cells by

incorporating gold nanospheres and nanorods into organic layers

# Xiaoyan Xu,<sup>a</sup> Aung Ko Ko Kyaw,<sup>b</sup> Bo Peng,<sup>c</sup> Qingguo Du,<sup>d</sup> Lei Hong,<sup>a</sup> Hilmi Volkan Demir,<sup>ac</sup> Terence K. S. Wong,<sup>\*a</sup> Qihua Xiong<sup>\*ac</sup> and Xiao Wei Sun<sup>\*a</sup>

 <sup>a</sup> NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore.
<sup>b</sup> Institute of Materials Research and Engineering (IMRE), Agency for Science Technology and Research (A\*STAR), Singapore 117602, Republic of Singapore
<sup>c</sup> School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 639798, Singapore
<sup>d</sup> Institute of High Performance Computing , 1 Fusionopolis Way, #16-16 Connexis North, Singapore 138632, Republic of Singapore

E-mail:ekswong@ntu.edu.sg

## **Experimental**

#### Synthesis of Au nanospheres and Au-silica nanorods

Au nanospheres were synthesized by rapid injection of 20 ml 38.8mM sodium citrate into a boiling growth solution of HAuCl<sub>4</sub> (200 ml, 1mM) under vigorous stirring. After boiling for 15 min, the solution was cooled to room temperature. The Au nanospheres solution (20)ml) was added to the mixed solution of hexadecyltrimethylammonium bromide (CTAB) (20ml, 0.2M) and HCl (0.8ml, 1M) under vigorous stirring at 30 °C. After the solution were kept for 24 h, CTAB-coated Au nanospheres were obtained. After a further 12 h at 0 °C, the CTAB was removed by centrifugation. Finally, the Au nanospheres were dispersed into water. The syntheses of Au-silica nanorods followed the seed-mediated method in our previous report.

#### **Device fabrication**

Indium tin oxide (ITO)-coated glass substrates (10 Ohm/square) were sequentially cleaned in detergent, deionized water, acetone and isopropyl alcohol under sonication for 15 min each. The substrates were then dried under a flow of nitrogen and treated with UV ozone for 10 min. To prepare the buffer layers, a Au nanospheres solution was doped into Poly(3,4-ethylene-dioxythiophene): poly(styrenesulphonate) (PEDOT:PSS) (Baytron P 4083). The PEDOT:PSS solutions with weight ratio of 0 wt%, 1.5 wt% 0.3 wt% and 0.6 wt% Au nanospheres were spin-coated at 5000 rpm for 40 s on ITO substrates and annealed at 150 °C in air for 20 min. The thicknesses of PEDOT:PSS films were both around 30 nm determined by a surface profiler, indicating that incorporation of Au nanospheres does not change the PEDOT:PSS film thickness. Before spin-coating the active layers in glove box, 100 µl Au-silica nanorods solution or 100 µl CB solvent were added to 900  $\mu$ l p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM solution in CB with 4  $\mu$ l of 1,8 octanedithiol processing additive. The final solutions consisted of p-DTS(FBTTh<sub>2</sub>)<sub>2</sub> (21 mg/ml, 1material, Inc.) and PC<sub>70</sub>BM (14 mg/ml, Nano-C, Inc.) and Au-silica nanorods with weight ratio of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt%. In our best solar cells, the 0.3 wt% of Au nanospheres and 1 wt% of Au nanorods were doped in PEDOT:PSS and p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM respectively. The prepared solutions were heated at 90 °C for 15 min prior to spin-casting. The solution was spin-coated on the top of PEDOT:PSS layer and annealed at 80 °C for 10 min. The thicknesses of the active layers with and without Au-silica nanorods were around 100 nm. Finally, a top electrode consisting of 20 nm Ca and 100 nm Ag were deposited on the active layer under vacuum condition of  $1 \times 10^{-4}$  Pa in a thermal evaporator. All devices had an active area of 0.8 mm<sup>2</sup> and were encapsulated before taking out from the glovebox.

#### Fabrication of hole-only devices

To determine the impact of Au NPs incorporated into different layers on hole mobility, we fabricated the hole-only devices with the structures of ITO/PEODOT:PSS (with and without Au nanospheres)/ p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM (with and without Ausilica nanorods)/MoO<sub>3</sub> (10 nm)/Ag (100 nm). Dark *J-V* characteristics of the hole-only devices were measured and then fitted using the space-charge limited current (SCLC) model and the Mott-Gurney law that includes field-dependent mobility, is given by

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \frac{V^2}{L^3} \exp(\beta \sqrt{\frac{V}{L}})$$

Where J is the current density,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of the p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM blend;  $\mu_0$  is the zero-field mobility;  $V = V_{appl} - V_{BI} - V_{RS}$ ,  $V_{appl}$  is the applied voltage,  $V_{BI}$  is the built-in voltage which results from the difference in the work function of the two electrodes, and  $V_{RS}$  is the voltage across the contacts. L is the thickness of the active layer and  $\beta$  is the field activation factor.

#### **Device characterization**

Transmission electron microscope (TEM) of the Au nanospheres and Au–silica nanorods were performed using a JEOL 1400 TEM with an accelerating voltage at 100

kV. Absorption spectra were measured using an UV/vis/near-IR spectrophotometer (PerkinElmer Lambda 950) equipped with a 150 mm diameter integrating sphere. Atomic force microscopy (AFM) (Cypher S, Asylum Research) in the tapping mode was used to analyze the surface roughness of the films. The film thickness was determined by a surface profiler (KLA-Tencor P-10). The J-V measurement of the devices was conducted with a Keithley 2400 source meter unit under simulated 100 mW cm<sup>-2</sup> (AM 1.5G) irradiation from a solar simulator (Solar Light Co. Inc.). The incident photon to current conversion efficiency (IPCE) measurement system (PVE 300, Bentham) comprised a xenon lamp, a monochromator, a chopper, a lock-in amplifier and a calibrated silicon photodetector.

#### **FDTD simulation**

The electric field intensity distribution is obtained using finite-difference timedomain (FDTD) method, the simulation region in x, y and z directions are all nonperiodic. PML (Perfect Matched Layer) boundary condition are used in x, y and z directions. TFSF (Total Field Scattered Field) light source is used for single core-shell nanoparticle e-field simulations. The mesh size is set at 1.0 nm in order to get the accurate field distribution. 3D (3 dimensional) power monitor is used to obtain the electric field information for wavelengths at 680 nm.



Fig. S1 AFM height images for the PEDOT:PSS films ( a, b: without and with Au nanospheres) and the p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM films (c, d: without and with Au-silica nanorods).



**Fig. S2** (a) *J-V* characteristics of p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM BHJ solar cells with Au nanospheres concentrations of 0 wt%, 0.15 wt%, 0.3 wt% and 0.6 wt% in PEDOT:PSS layer and (b) *J-V* characteristics of p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM BHJ solar cells with Ausilica nanorods concentrations of 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt% in the active layer.