



# A plasmonically enhanced polymer solar cell with gold–silica core–shell nanorods

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## ABSTRACT

We report the use of chemically synthesized gold (Au)–silica core–shell nanorods with the length of  $92.5 \pm 8.0$  nm and diameter of  $34.3 \pm 4.0$  nm for the efficiency enhancement of bulk heterojunction (BHJ) polymer solar cells. Silica coated Au nanorods were randomly blended into the BHJ layers of these solar cells. This architecture inhibits the carrier recombination at the metal/polymer interface and effectively exploits light absorption at the surface plasmon resonance wavelengths of the Au–silica nanorods. To match the two plasmon resonant peaks of the Au–silica nanorods, we employed a low bandgap polymer, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) to construct a solar cell. The absorption spectrum of PCPDTBT:[6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM) is relatively wide and matches the two plasmon resonance peaks of Au–silica nanorods, which leads to greater plasmonic effects. We also constructed the poly(3-hexylthiophene):[6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (P3HT:PC<sub>60</sub>BM) cells for comparison. The absorption spectrum of P3HT:PC<sub>60</sub>BM only overlaps one of the plasmon resonance peak of Au–silica nanorods. The efficiency of the P3HT:PC<sub>60</sub>BM device incorporating optimized Au–silica nanorods is enhanced by 12.9% from 3.17% to 3.58%, which is due to the enhanced light absorption. Compared with the P3HT:PC<sub>60</sub>BM device with Au–silica nanorods, the PCPDTBT:PC<sub>70</sub>BM device with 1 wt% Au–silica nanorods concentration has a higher efficiency of 4.4% with an increase of 26%.

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## 1. Introduction

Polymer solar cells (PSCs) are a promising alternative to conventional silicon solar cells due to the low-cost materials, mechanical flexibility and solution processability at low temperature [1–6]. At present, the bulk heterojunction (BHJ) architecture based on blend of semiconducting poly-

mer (donor) and soluble fullerene derivative (acceptor), which greatly increases the interfacial area for efficient exciton dissociation, gives a reasonably high efficiency [7–12]. However, the active layer of such devices typically has to be very thin due to low carrier mobility and short exciton diffusion length of the organic semiconductor materials (5–20 nm) [13]. The optimum active layer thickness is limited to the range of 50–100 nm [13], which leads to poor light absorption. Therefore, a variety of light-trapping techniques are necessary for improving the light absorption efficiency and effective optical path length, such as new surface micro or nanostructuring techniques [14], optimization of the electromagnetic field [15] and realization of photonic crystals by bulk structuring [16].

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It is necessary to increase the light absorption by the BHJ film without increasing the film thickness. Recently, metallic nanostructures that support surface plasmons have been intensively investigated due to the light scattering and localized surface plasmon resonance (LSPR) effects [17–20]. Excited surface plasmons enhance the local electric field intensity distribution around the nanostructures, which leads to the light absorption enhancement in the active layer [21]. The LSPR is excited when the frequency of the incident light matches the LSPR peak of metallic nanoparticles (NPs). The surface plasmon resonance frequency depends strongly on the size, shape, type of metal and the dielectric environment of metallic NPs [21–27]. In addition, for large metallic NPs (~100 nm) within the BHJ layer, the incident photons can be scattered strongly by metallic nanostructures into a longer propagation path in the active layer. Recently, both theoretical and experimental studies on plasmonic effects in organic and inorganic photovoltaic devices have shown interesting results [9,28,29]. Theoretically, broadband optical absorption enhancement from the LSPR effect had been verified by simulation with three dimensional finite-difference time-domain method [17]. Blending metallic NPs into the active layer could lead to multiple light scattering effect within the BHJ layer and reduce the cell resistance. However, rapid recombination of the photo-generated charge carriers will occur at the surface of bare metallic NPs because of a high surface recombination velocity [24]. In order to avoid this issue, most experimental studies embedded bare metallic NPs in the poly(3,4-ethylene-dioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) soluble conducting polymer or positioned them at the interface of the indium tin oxide (ITO) coated glass substrates [9,28,30,31]. So far, the investigation on PSCs with metallic NPs blended into the BHJ layer has been limited [32–34]. Recently, gold (Au) NPs coated by a thin shell of silica were introduced into dye-sensitized solar cells (DSSC) [35]. The silica shell can efficiently prevent charge recombination and realize multiple light reflections in the active layer of DSSC. In addition, most existing studies on metallic nanostructures for plasmonic enhancement effects are focused on spherical NPs with a diameter of less than 50 nm [18].

In this work, we investigate the effect of Au–silica core–shell nanorods on PSCs based on the blend of poly(3-hexylthiophene):[6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (P3HT:PC<sub>60</sub>BM) and the blend of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]:[6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PCPDTBT:PC<sub>70</sub>BM). The Au–silica nanorods were blended directly into a BHJ solution with different concentration. We demonstrate that Au–silica nanorods have a stronger influence on PSCs based on low bandgap polymer PCPDTBT than PSCs based on P3HT.

## 2. Experimental

### 2.1. Synthesis of Au–silica core–shell nanorods

Au nanorods were synthesized by a seed-mediated method [36]. First, the Au seed solution was prepared by

borohydride reduction of 0.25 mM HAuCl<sub>4</sub> in an aqueous hexadecyltrimethylammonium bromide (CTAB) solution (10 mL, 0.1 M). For the synthesis of the Au nanorods, 10 μL of seed solution was added to an aqueous solution of HAuCl<sub>4</sub> (0.01 M, 2 mL), AgNO<sub>3</sub> (0.01 M, 0.4 mL), CTAB (0.1 M, 40 mL), ascorbic acid (0.1 M, 0.32 mL) and HCl (1.0 M, 0.8 mL). After mixing by gentle inversion for 10 s, the reaction solution was left undisturbed for 16 h. The Au nanorods were obtained by centrifugation and re-dispersed in 26.7 mL of deionized water.

Au–silica core–shell nanorods were synthesized according to a previously published procedure [37]. NaOH solution (0.1 M) was added to 2 mL of Au nanorods solution until the pH value was adjusted to 10–11. A 20 vol% solution of tetraethyl orthosilicate (TEOS) in methanol was then added (60 μL for Au nanorods). After stirring for 12 h, Au–silica core–shell nanorods were obtained by centrifugation, and re-dispersed in 3 mL ethanol. Finally, 50 μL of hexadecyltrimethoxysilane was added to obtain the core–shell solution. After stirring for 18 h at 60 °C, the hydrophobic core–shell nanostructures were obtained by centrifugation and re-dispersed in chlorobenzene (CB) or 1, 2-dichlorobenzene (DCB). The reason for dispersing the Au–silica nanorods in two separate solvents is to avoid possible co-solvent effects during fabrication of the PSC devices.

### 2.2. Device fabrication

The device structures are ITO/PEDOT:PSS/P3HT:PC<sub>60</sub>-BM/Ca/Al and ITO/PEDOT:PSS/PCPDTBT:PC<sub>70</sub>BM/Ca/Al (Fig. 1). ITO coated glass substrates with a sheet resistance of 15 Ω/□ were cleaned for 15 min respectively in detergent, de-ionized water, acetone and isopropyl alcohol using an ultrasonic bath and blown dry using nitrogen. The substrate was then treated with an oxygen plasma for 3 min. PEDOT:PSS (Baytron P 4083) was spin coated at 3000 rpm for 60 s onto the ITO electrode with a thickness of ~40 nm. The ITO coated glass substrate with the PEDOT:PSS layer was then preheated on a hotplate at 150 °C for 20 min in air. A 40 mg blend of P3HT (Rieke Metals, Inc.) and PC<sub>60</sub>BM (American Dye Sources, Inc.) with a weight ratio of 1:0.8 was dissolved in 1 mL of DCB to achieve a concentration of 40 mg/mL. For the P3HT:PC<sub>60</sub>-BM device with Au–silica nanorods, the Au–silica nanorods dispersed in DCB was diluted by adding DCB to give a 1 mL

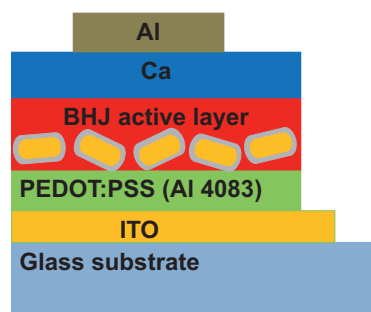


Fig. 1. Schematic of polymer solar cell with Au–silica nanorods in BHJ layer.

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