Influence of SiO$_2$ shell thickness on power conversion efficiency in plasmonic polymer solar cells with Au nanorod@SiO$_2$ core-shell structures

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Locating core-shell metal nanoparticles into a photoactive layer or at the interface of photoactive layer/hole extraction layer is beneficial for fully employing surface plasmon energy, thus enhancing power conversion efficiency (PCE) in plasmonic organic photovoltaic devices (OPVs). Herein, we first investigated the influence of silica shell thickness in Au nanorods (NRs)@SiO$_2$ core-shell structures on OPV performances by inserting them into poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) and thiene[3,4-b]thiophene/benzodithiophene (PTB7) interface, and amazedly found that a 2–3 nm silica shell onto Au NRs induces a highest short-circuit current density of 21.2 mA cm$^{-2}$ and PCE of 9.55%. This is primarily due to an extremely strong local field and a much slower attenuation of localized surface plasmon resonance around ultrathin silica-coated Au NRs, with which the field intensity remains a high value in the active layer, thus sufficiently improves the absorption of PTB7. Our work provides a clear design concept on precise control of the shell of metal nanoparticles to realize high performances in plasmonic OPVs.

Organic photovoltaic devices (OPVs) have attracted a considerable attention because of their advantages of light-weight, low-cost, large-scale manufacturing process and mechanical flexibility$^{1,2}$. Unfortunately, in order to achieve efficient carrier extraction, the photoactive layer in OPVs must be rather thin (100 nm or less) due to their extremely low carrier mobilities for most of organic/polymer materials (on the order of $10^{-4}$ cm$^2$/V·s). Such thin photoactive layers lead to a significant loss of incident sunlight, thereby a final low light absorption efficiency and power conversion efficiency (PCE). Recently, surface plasmons (SPs) have been widely employed in OPVs to significantly improve the light harvesting in photoactive layers and hence enhance short-circuit current density ($J_{sc}$) and PCEs via amplifying local field and scattering incident sunlight$^{3,4}$.

Both periodic/aperiodic metal nanoarrays$^{3-7}$ and discrete metal nanoparticles$^{8-15}$ were used to generate SPs, and the latter was widely reported due to ease fabrication with a variety of shapes (e.g., nanospheres$^{8,9}$, nanoprisms$^{10}$, nanorods (NRs)$^{11-13}$ and nanocubes)$^{14,15}$. Among all kinds of nanoparticles, both Au nanocubes and Au NRs generate a much stronger localized surface plasmon resonance (LSPR) than the other shapes. But very unfortunately, the local field around Au nanocubes declines very quickly (Figure S1 in Supplementary Information), and doping them into a carrier extraction layer leads to an extremely limited increase in PCE (e.g., only 9.3%)$^{14}$. In contrast to Au nanocubes, Au NRs show a much slower decline in the local field intensity and their adjustable...
of gold nanoparticles into the active layer, generating an increase of 15.5% in efficiency for PCPDTBT:PC 71BM cells, realizing 12.9% and 26% enhancement factors for PCE. It is worth noting that the direction of the energy transfer is dependent on the SiO 2 thickness. Although he did not fabricate any device, his research work on the physical mechanism of the energy transfer indicates the SiO2 thickness plays an important role in energy transfer directions. So in our present paper, we chose Au NRs with a longitudinal/transverse ratio of ~2.0 and then wrapped these NRs in 3, 14 and 38 nm SiO2 shells. Note that a longitudinal/transverse ratio of ~2 generates a long/short axis resonance of 608/520 nm in aqueous solution and even if transferring these NRs into a solid film, the red shift for the longitudinal axis resonance is within 50–60 nm, with these NRs absorption still being located within the absorption range of the photoactive layer. By inserting these NRs at the PEDOT:PSS/PTB7 interface. As the simulated film absorption shown in Fig. 1, we observed a more obvious absorption occurs in the PTB7:PC71BM layer and obtained a PCE of 8.72% with a 31% enhancement over the control device. It should be noted here the thickness of the silica shell layer is 7 nm in their surface plasmon-enhanced OPVs. Then they investigated thickness influences of silica shells located them into PEDOT:PSS in OPVs. The thick silica shell layer makes these nanospheres penetrate into 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-C71-butyric acid methyl ester (PCPDTBT:PC71BM) cells, realizing 12.9% and 26% enhancement factors for PCE. It is worth noting that they did not mention the thickness of the silica shell in their paper. In their following work, they fabricated a dual plasmonic OPV by respectively doping Au nanospheres and Au-silica nanorods into PEDOT:PSS and the 7,7′-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b’]-dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-2,2′-bithiophen)-5-yl)benzo[1,2,5]thiadiazole) (p-DTS(FBTTh2):PC71BM layer and obtained a PCE of 9.55% PCE and a 21.2 mA cm−2 Jsc, realizing a 9.55% PCE and a 21.2 mA cm−2 Jsc. To our knowledge, this is the best result using a single kind of metal nanoparticles in plasmonic OPVs.

Results

Before synthesizing Au core-shell nanoparticles and manufacturing plasmonic OPVs, we first simulated the absorption power of the active layers by locating Au NR@SiO2 with alterable SiO2 shell thicknesses at the PEDOT:PSS/PTB7 interface. As the simulated film absorption shown in Fig. 1, we observed a more obvious absorption occurs in the PTB7:PC71BM layer with a thinner silica shell layer. It is especially significant at 750–850 nm with a peak of ~810 nm when the silica layer is no more than 14 nm. As Hsiao’s report, the resonance wavelength near the cutoff wavelength of the PTB7 donor will be very beneficial for enhancing the light absorption ability of the photoactive layer. In order to verify this point and simultaneously observe the influence of the silica shell thickness on PCE, we synthesized Au NR core-shell nanostructures with different SiO2 thicknesses,
e.g., 3, 14, and 38 nm, with their transmission electron microscope (TEM) images shown in Fig. 2. Analysis on ~380 Au NRs without silica coatings, we gave the detailed statistics data on the longitudinal/transverse ratios, as the histogram shown in Fig. 3a. We found that it mainly consists of rod shape nanoparticles with longitudinal/transverse ratios of $2.0 \pm 0.5$, among which ~43% particles own a longitudinal/transverse ratio of $2.0 \pm 0.1$, demonstrating a good homogeneity in our nanoparticles. These Au NRs were further wrapped with silica thicknesses of about $3 \pm 0.6$, $14 \pm 2$ and $38 \pm 5$ nm by adding different volumes of tetraethylorthosilicate (TEOS) into the final nanorods solutions. The as-synthesized Au NRs with $3 \pm 0.6$, $14 \pm 2$, and $38 \pm 5$ nm silica shells are shown in Fig. 2b–d, from which we find dense and uniform silica coatings on Au NRs. And these dense and uniform silica coatings sufficiently avoid exciton quenching through an efficient isolation of excitons from NRs. With the increase in silica coating thickness, the absorption for Au NR’s longitudinal axis exhibits an obvious red shift from 608 nm (without silica shell) to 635 nm (38 nm silica shell), as shown in Fig. 3b, and this trend is in accordance with previous reported results. In contrast, the absorption of the transverse axis shows an ignorable

**Figure 2.** The TEM images for Au NRs coated with (a) 0, (b) 3, (c) 14, and (d) 38 nm silica shells.

**Figure 3.** (a) The statistics data on the longitudinal/transverse ratios of as-synthesized Au NRs, and (b) the absorption spectra of the Au NRs with different silica shells.
alteration with the resonance wavelength mainly locating at ~520 nm (520, 522 and 524 nm for 3, 14 and 38 nm silica shells).

To fully use the magnified local field and light scattering induced by these gold surface plasmons, we'd better locate these metal nanoparticles into an active layer or at the interface of carrier extraction layer/photoactive layer. In our previous experiments, we found physically doping metal nanoparticles into a photoactive layer, especially in PTB7:PC71BM blend solution, brings some negative effects on the micromorphology of the photoactive film (e.g., phase separation)27, leading to a decline in PCE although these metal nanoparticles are covered with dielectric shells. So in the present work, we inserted Au NR@SiO2 core-shell nanostructures at the interface of PEDOT:PSS/PTB7:PC71BM to try to reduce the negative influence of these nanoparticles on the film morphology of the PTB7:PC71BM active layer. Although Au NRs@SiO2 were spincoated onto PEDOT:PSS before forming PTB7:PC71BM, they were almost totally surrounded by the following PTB7:PC71BM photoactive layer in our device structure, which indicates a large part of the plasmon-enhanced electric field can be absorbed by the photoactive layer.

Through experimental exploration, we found the optimal distribution density for Au NRs@SiO2 is about one nanoparticle/2–3 μm2. We observed all plasmonic devices generate enhancements in PCE, among which the solar cell with 3 nm silica shell-coated Au NRs shows maximum enhancement factors of 27% and 28.5% for PCE and $J_{sc}$, compared with the reference device without any nanoparticles (Fig. 4a and Table 1). This generates a PCE of as high as 9.55% (with a maximum value of 9.61%) in the OPV doped with Au NRs@3 nm SiO2, reaching a highest PCE level among reported plasmonic OPVs using a single kind of metal nanoparticles28,29. Increasing the SiO2 shell to 38 nm significantly declines PCE and $J_{sc}$ to 8.25% and 18.5 mA cm$^{-2}$, with only 9.3% and 12.1% enhancements. We summarized all parameters including $V_{oc}$, $J_{sc}$, FF, PCE, series resistance ($R_s$) and shunt resistance ($R_{sh}$) in Table 1, from which we noted that although doping a proper concentration of Au NRs brings a negligible effect on $V_{oc}$ and FF, it greatly enhances $J_{sc}$.

**Discussion**

Significant increase in $J_{sc}$, on one hand, is attributed to the scattering effect of Au NRs@SiO2 to the incident solar light, thus giving rise to a longer light path and further improving light absorption in OPVs12,30 and on the other hand, is due to an obviously enhanced local field induced by Au NRs LSPR, promoting a further absorption of the active layer. Here, we calculated the electromagnetic field inside the cells in order to make sure of the role that the Au NRs played. It should be noted that only electric field intensity is considered due to a far larger intensity for the electric field than the magnetic one. Referring to the relative position of Au NRs in the solar cells in Fig. 5a (with Au NRs longitudinal axis and light propagation direction respectively along X- and Z-axes), we compared the change of the electric field intensities with or without Au NRs@SiO2 at different wavelengths, with the simulation results shown in Fig. 5b–d, and drew some conclusions. Here, we supposed that the Au NRs distribute periodically along with XY plane and one of Au NRs runs across the center of our present coordinate system (this Au NR@SiO2’s center is located at 0 for X, Y, and Z axes). First, we found a maximum field in XZ plane at $X = 0$ occurs at 653 and 765 nm for 38 and 3 nm SiO2-coated Au NRs, reaching a highest peak among reported plasmonic OPVs using a single kind of metal nanoparticles20,25. Increasing the SiO2 shell to 38 nm significantly declines PCE and $J_{sc}$ to 8.25% and 18.5 mA cm$^{-2}$, with only 9.3% and 12.1% enhancements. We summarized all parameters including $V_{oc}$, $J_{sc}$, FF, PCE, series resistance ($R_s$) and shunt resistance ($R_{sh}$) in Table 1, from which we noted that although doping a proper concentration of Au NRs brings a negligible effect on $V_{oc}$ and FF, it greatly enhances $J_{sc}$.

**Table 1.** Photovoltaic parameters for devices with and without Au NRs@SiO2.

| SiO2 thickness (nm) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) | $R_s$ (Ω cm$^2$) | $R_{sh}$ (Ω cm$^2$) |
|--------------------|-------------|---------------------|-----|---------|----------------|------------------|
| ref.               | 0.74        | 16.5                | 0.60| 7.52    | 10.1           | 801              |
| 3 ± 0.6            | 0.74        | 21.2                | 0.60| 9.55    | 7.4            | 923              |
| 14 ± 2             | 0.74        | 19.1                | 0.60| 8.53    | 8.7            | 322              |
| 38 ± 5             | 0.74        | 18.5                | 0.60| 8.25    | 7.8            | 435              |

**Figure 4.** (a) $J$–$V$ curves, (b) diode curves under dark conditions and (c) IPCE characteristics with and without Au NRs@SiO2 core-shell structures.
be sufficiently used in the case with a thick silica shell and in contrast, the field remains a high level in the active layer when employing an ultrathin SiO₂ shell. Thus, we should cover a shell as thin as possible onto metal nanoparticles to sufficiently utilize the Au-induced LSPR and 2–3 nm is the thinnest shell layer that we can control in our present experimental conditions. A shell of less than 2 nm will generate incomplete coverage, which leads to a significant exciton quenching on the surfaces of these Au NRs. Second, from the field distributions in XZ plane (at Y = 0) and along with Z axis shown in Figs 5 and 6, we mentioned that the local field induced by Au NRs@SiO₂ is asymmetrical along with the propagation direction of the incident light (Z axis). For instance, the local field at the contact surface of Au NRs@SiO₂ and PEDOT:PSS (Z = −47 nm in the top structure of Fig. 5a) is larger than that at the interface of Au NRs@SiO₂ and PTB7 at Z = +47 nm, which is especially obvious at 765 (Fig. 5c) and 804 nm (Fig. 5d, 804 nm is near the cut-off absorption wavelength of PTB7) for Au NRs with a 38 nm shell layer. Via promoting the PTB7 absorption near the bottom of nanoparticles at the PEDOT:PSS side, together with light scattering of Au NRs@SiO₂, it generates a final 9.7% increase in PCE for the device with 38 nm SiO₂-coated Au NRs. The measured absorption and PL spectra for the PEDOT:PSS/Au NRs@SiO₂/PTB7:PC₇₁BM multilayer in Fig. 7 is accordant with the above simulated results, with the 3 nm silica-coated Au NRs-inserted multilayer films showing a strongest light absorption ability and a highest PL intensity. Analysis on the simulated electric field distributions around Au NRs@SiO₂ core-shell structures, we found the maximum value occurs at the nanorod’s shoulder (Fig. 6), instead of its sides discussed above, so we clearly observed the maximum LSPR intensity, generated by a thin silica shell layer of 3 nm, reaches ~2500, far larger than ~350 and ~600 for 14 and 38 nm silica shells. As a result, an extremely strong local field and a much slower attenuation of LSPR around 3-nm silica-coated Au NRs make the field intensity remain a high value even in the active layer, thus sufficiently improve the absorption of PTB7, accompanied with significant increases in Jₜₒ and PCE.

Figure 5. (a) The cross-section schematic of the plasmon-enhanced OPVs along Z axis (at Y = 0). Au NRs@SiO₂ with 3, 14 and 38 nm silica shells are located in different coordinate positions in order to simulate the field distribution easily, where the PTB7:PC₇₁BM active layer runs across the Z axis range of −12−88, −23−77 and −47−53 nm for doping Au NRs@SiO₂ with 3, 14 and 38 nm silica shells. The PTB7:PC₇₁BM layer without any Au NRs@SiO₂ is located within −12−88 nm. The electric field distributions along with Z axis (both X = 0 and Y = 0) are calculated with FDTD software. (b–d) Respectively corresponds to 653, 765, and 804 nm and in each graph, it corresponds to the electric fields with 38, 14, 3 nm silica shell thicknesses from top to down. The bottom one is the electric fields without nanoparticles. Inset is the electric field intensity penetrated into the active layer.
In addition to the change of electromagnetic field inside OPVs, we also considered influences of Au NRs@SiO2 core-shell structures on the electrical transport properties of films. From Table 1, we found inserting Au NRs induces a slight decrease in $R_s$, and it should be attributed to a beneficial influence of ethanol solvent instead of Au NRs31. In order to explain this problem, we investigated the influence of the ethanol solvent on OPV's performance, where ethanol was used as Au NRs' solvent in our plasmonic OPVs. We manufactured two groups of devices with a standard structure of ITO/PEDOT:PSS/PTB7:PC71BM/LiF/Al, and an ethanol-treated one with ethanol spincoated onto PEDOT:PSS (2000 rpm, same with metal nanoparticles' rotation speed). The introduction of ethanol into the PEDOT:PSS/PTB7:PC71BM interface brings significant increases in FF and $J_{sc}$, followed by a PCE increase, indicating a more efficient exciton dissociation in ethanol-treated device, as the summarized parameters ($J_{sc}$, PCE, FF, $R_s$ and $R_{sh}$) in Figure S2 in Supplementary Information. The use of ethanol also results in a decline in $R_s$. Thus, as a combination of positive and negative effects from ethanol and core-shell metal nanoparticles, $R_s$ was finally observed to slightly decline in plasmonic OPVs, as shown in Table 1. In addition, $R_{sh}$ was also observed with a slight increase and then a significant decline accompanied with the silica shell thickness. This means that a thicker silica shell onto metal nanoparticles on one hand restrains carrier transport due to a longer

Figure 6. The local field distributions around Au NRs in plasmonic devices on XZ plane at $Y = 0$. Here, incident light propagation and polarized direction of this incident light beam are along Z and X axis, respectively. (a,d,g) Correspond to the fields at 653, 765, and 804 nm for Au NRs with 3 nm silica shells, (b,e,h) correspond to the fields at 653, 765, and 804 nm for Au NRs with 14 nm silica shells, while (c,f,i) correspond to the fields at 653, 765, and 804 nm for Au NRs with 38 nm silica shells.

Figure 7. The measured (a) absorption and (b) PL spectra of the PEDOT:PSS/Au NRs@SiO2/PTB7:PC71BM films with 3, 14, and 38 nm silica shells. A standard structure of PEDOT:PSS/PTB7:PC71BM is also attached for comparison.
transport path for these dissociated excitons to overcome (from nanoparticle's surface to the PEDOT:PSS layer), and on another hand leads to a thinner PTB7:PC\textsubscript{71}BM photoactive layer on these Au NRs, both of which make photon-generated excitons obviously decline with shell thickness' increase. The calculated exciton generation rates in control device and plasmonic OPVs with 3, 14 and 38 nm silica thicknesses are $1.11 \times 10^{28}$, $1.39 \times 10^{28}$, $1.28 \times 10^{28}$, and $1.26 \times 10^{28}$ m$^{-3}$ s$^{-1}$ at saturation current densities of 177.5, 223.0, 204.6, and 202.3 A m$^{-2}$, respectively. Detailed results are shown in Figure S3 in Supplementary Information. Above explanations also make it clear that a slight decline in the dark current density in plasmonic OPVs (Fig. 4b).

Finally, the surface morphologies of the active layers with three kinds of Au NRs@SiO\textsubscript{2} were measured by applying atomic force microscopy (AFM), where the PTB7:PC\textsubscript{71}BM film without metal nanoparticles was also measured for comparison, as can be seen in Fig. 8. The employment of Au NRs@SiO\textsubscript{2} aroused some changes of the surface roughness ($R_{\text{ms}}$) of the active layer, with a gradual increase in $R_{\text{ms}}$ from 0.58 nm for the pure PTB7:PC\textsubscript{71}BM film to 0.76, 1.00, and 1.17 nm for the films inserted with Au NRs with 3, 14, and 38 nm SiO\textsubscript{2} shells. The increase in surface roughness may enlarge the interface contact area of the PEDOT:PSS/active layer and the active layer/cathode, which is beneficial to exciton dissociation and electron extraction\textsuperscript{8,11}, thus enhances $J_{sc}$ and FF. However, constant values of FF in our measurement results demonstrate the insertion of Au NRs at the interface of PEDOT:PSS/active layer generates an ignorable influence on the exciton dissociation, suggesting a major mechanism on performance improvements is originated from absorption enhancement induced by SPs.

Conclusions

As a result, we synthesized Au nanorods with different silica shell thicknesses and inserted them into the interface of PEDOT:PSS and PTB7:PC\textsubscript{71}BM. And we amazedly found the OPVs doped with Au NRs within a silica shell of as thin as 2–3 nm exhibit the highest $J_{sc}$ and PCE. This is primarily due to an extremely strong local field generated by Au NRs with a thin silica shell. In addition, a much slower attenuation of LSPR around Au NRs@ 3 nm SiO\textsubscript{2} makes the local field intensity remain a high value in the active layer, thus sufficiently improves the absorption of PTB7. We also explored the influence of the SiO\textsubscript{2}-coated Au NRs on film's electrical property and found doping Au NRs@SiO\textsubscript{2} slightly reduces the electrical conductivity ability of films. Our exploration work provides a clear design concept on precise control of core-shell metal nanoparticle's shell thickness to realize high performances in plasmonic OPVs.

Methods

Materials. The following chemicals were purchased and used as received. Hexadecyltrimethylammonium bromide (CTAB, > 98.0%), tetrachloroaurate trihydrate (H\textsubscript{AuCl\textsubscript{4}}·3 H\textsubscript{2}O), sodium borohydride (NaBH\textsubscript{4}, 99%) and L-ascorbic acid (AA, > 99.5% from BioUltra) were purchased from J&K Chemical. Sodium 3-methylsalicylate
(>97.0%) were purchased from TCI America. Silver nitrate (AgNO₃, >99%), tetraethylorthosilicate (TEOS, 99%), 1,8-diiodoctane and Al were purchased from Sigma Aldrich. PEDOT:PSS (AI 4083), PTB7, PC₇₁BM and LiF were bought from Baytron P, I-Material, Nano C, and Hanfeng Chemical, respectively. Ultrapure water was produced with a Milli-Q Integral 5 system and used in Au NR synthesis experiments. All glassware were cleaned with aqua regia, rinsed extensively with water, and dried in an oven before use.

**Synthesis of Au NRs.** The seed solution for Au NRs was prepared as previously reported.²⁻ 5 mL of 0.5 mM HAuCl₄ was mixed with 5 mL of 0.2 M CTAB solution. 0.6 mL of fresh 0.01 M NaBH₄ was diluted to 1 mL with water and was then injected into above Au(III)—CTAB mixture solution under vigorous stirring (1200 rpm). The solution color changed from yellow to brownish-yellow, and the stirring was stopped after 2 min. The seed solution was aged at room temperature for 30 min before use.

To prepare the growth solution, 0.28 g of CTAB together with 0.05 g sodium 3-methylsalicylate were dissolved in 10 mL of warm water (60 °C) in a 50 mL Erlenmeyer flask. The solution was allowed to cool to 30 °C, when a 240 μL of 4 mM AgNO₃ solution was added. The mixture was kept undisturbed at 30 °C for 15 min, after which 10 mL of 1 mM HAuCl₄ solution was added. After 15 min of slow stirring (400 rpm), a 50 μL of 0.64 M AA was added, and the solution was vigorously stirred for 30 s until it became colorless. The growth solution with a CTAB concentration of about 0.05 M was used right after preparation. Finally, 32 μL of seed solution was injected into the growth mixture. The resultant growth solution was stirred for 30 s and left undisturbed at 30 °C for 12 h for Au NRs growth. The reaction products were further treated with a centrifugation of 8500 rpm for 25 min to remove the raw materials.

**Synthesis of Au NR@SiO₂.** To coat the Au NRs with SiO₂, 0.1 mM of NaOH solution was added into 5 mL of Au NRs solution to adjust the pH value to 10–11. Then TEOS was added to the solution under gentle stirring and the reaction was allowed to proceed for approximately 12 h in 90 °C. Adding 3, 10 and 15 μL of TEOS to the nanorods solutions generated the silica shell thicknesses of about 3 ± 0.6, 14 ± 2 and 38 ± 5 nm, respectively. The Au@SiO₂ core@shell nanostructures were finally obtained with a centrifugation of 8500 rpm for 15 min to remove the surfactant and then re-dispersed into 5 mL ethanol.

**Plasmonic OPV device fabrication.** OPVs were fabricated on a 180 nm-thick indium tin oxide (ITO)-coated glass substrate as our previously reported procedure.²⁸ Pre-patterned ITO coated glass substrates (7 Ω/square) were cleaned in sequence with acetone, ethanol, and deionized water for 10 min, and then blown with a N₂ gas. After a 100 °C heat treatment for 20 min, the substrates were treated with UV O₃ for 7 min and then transferred onto a spincoater to form a ~40 nm PEDOT:PSS layer, followed by a dry process of 120 °C for 30 min. The ethanol solvent consisting of Au NR@SiO₂ core@shell nanostructures were spin-coated onto the PEDOT:PSS film with different doping concentrations of nanoparticles to form an optimized distribution density. After that, the PTB7:PC₇₁BM blend layer was spin-coated onto the PEDOT:PSS at 1100 rpm for 60 s, forming a film of ~100 nm. Note that PTB7 and PC₇₁BM were mixed with a weight ratio of 10:15 mg in 1 ml chlorobenzene solvent and the additive 1,8-diiodoctane was then added into the mixture solution with a volume ratio of 3:97. The above blend solution was stirred for about 2 days before use. With a solvent drying for about 0.5 h, the active layer-coated samples were transferred into the vacuum chamber to thermally deposit a thin LiF and a thick Al cathode at 200 °C for 10 s and 10 min, respectively. The LiF were bought from Baytron P, 1-Material, Nano C, and Hanfeng Chemical, respectively. Ultrapure water was used to prepare HNO₃. The water and was then injected into above Au(III)—CTAB mixture solution under vigorous stirring (1200 rpm). After a 100 °C heat treatment for 20 min, the substrates were treated with UV O₃ for 7 min and then transferred onto a spincoater to form a ~40 nm PEDOT:PSS layer, followed by a dry process of 120 °C for 30 min. The solution color changed from yellow to brownish-yellow, and the stirring was stopped after 2 min. The seed solution was aged at room temperature for 30 min before use.

To prepare the growth solution, 0.28 g of CTAB together with 0.05 g sodium 3-methylsalicylate were dissolved in 10 mL of warm water (60 °C) in a 50 mL Erlenmeyer flask. The solution was allowed to cool to 30 °C, when a 240 μL of 4 mM AgNO₃ solution was added. The mixture was kept undisturbed at 30 °C for 15 min, after which 10 mL of 1 mM HAuCl₄ solution was added. After 15 min of slow stirring (400 rpm), a 50 μL of 0.64 M AA was added, and the solution was vigorously stirred for 30 s until it became colorless. The growth solution with a CTAB concentration of about 0.05 M was used right after preparation. Finally, 32 μL of seed solution was injected into the growth mixture. The resultant growth solution was stirred for 30 s and left undisturbed at 30 °C for 12 h for Au NRs growth. The reaction products were further treated with a centrifugation of 8500 rpm for 25 min to remove the raw materials.

**Synthesis of Au NR@SiO₂.** To coat the Au NRs with SiO₂, 0.1 mM of NaOH solution was added into 5 mL of Au NRs solution to adjust the pH value to 10–11. Then TEOS was added to the solution under gentle stirring and the reaction was allowed to proceed for approximately 12 h in 90 °C. Adding 3, 10 and 15 μL of TEOS to the nanorods solutions generated the silica shell thicknesses of about 3 ± 0.6, 14 ± 2 and 38 ± 5 nm, respectively. The Au@SiO₂ core@shell nanostructures were finally obtained with a centrifugation of 8500 rpm for 15 min to remove the surfactant and then re-dispersed into 5 mL ethanol.

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Author Contributions
R.Z., S.F.C. and L.P. designed, fabricated and characterized the devices. R.Z. and Y.F.Z. synthesized the Au NRs@SiO₂. S.F.C. conducted the optical simulation. X.L., X.M.F., Y.Q.G. and W.H. discussed the results and commented on the manuscript, and S.F.C. and R.Z. wrote the manuscript.

Additional Information
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