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Investigation of a gold quantum dot/plasmonic gold nanoparticle system for improvement of organic solar cells†

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Light management allows enhancement of light harvesting in organic solar cells (OSCs). In this paper, we describe the investigation of OSCs enhanced by the synergistic effect of gold quantum dots (AuQDs) and localized surface plasmons, obtained by blending a AuQD layer and plasmonic gold nanoparticles (AuNPs) in a hole-transport layer (HTL). Different AuQDs emitting blue, green, and red fluorescence were examined in this study. The OSCs were demonstrated to comprise an ITO-coated glass substrate/AuQDs/PEDOT:PSS:AuNPs/P3HT:PCBM/Al structure. The UV-visible spectra, current density versus voltage characteristics, impedance spectra, and incident photon-to-current efficiency of the fabricated devices were evaluated. The results showed an enhancement of photovoltaic efficiency achieved as a result of the increase in short-circuit current density (J_{sc}) and power conversion efficiency (PCE) in comparison with those of the reference OSCs. The best synergistic effect was found with OSCs consisting of a green-emitting AuQD layer and a HTL containing AuNPs, resulting in the highest improvement in PCE of 13.0%. This indicated that the increase in light harvesting in the developed devices was induced by extended light absorption in the UV region resulting from absorption by the AuQD layer and emission of visible fluorescence from the AuQD layer to the photoactive layers. Moreover, the localized surface plasmon effect of AuNPs, which also contributed to an increase in light trapping in the proposed OSCs, was enhanced by the effect of the AuQDs.

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Introduction

Organic thin-film solar cells (OSCs) are being considered as a promising alternative renewable energy source due to their excellent properties, such as low weight and high flexibility, and the feasibility of low temperature processing, solution-based fabrication, and cost-effective production of OSCs.^{1–3} Although bulk heterojunction (BHJ) OSCs exhibited several advantages

and improved the performance of photovoltaic devices, the short carrier diffusion length of polymer materials limits the film thickness of the active layer in the OSCs, resulting in lower power conversion efficiency (PCE) compared with that of traditional solar cells based on crystalline Si.^{1,4} Metallic nanostructure-induced plasmonic properties have been used to improve light harvesting in photovoltaic devices;^{5–8} in particular, the introduction of gold nanoparticles (AuNPs) into OSCs enhanced the photocurrent and PCE.^{9–18} We also reported the use of urchin-like AuNPs to improve the performance of OSCs.⁹ Plasmonic nanoparticles (NPs) are usually dispersed in photoactive or hole-transport layers as well being deposited at the interfaces of organic layers in photovoltaic devices.^{19,20} AuNPs with particle sizes from 2 to 100 nm typically enhance the electric field and optical absorption through excitation of localized surface plasmon resonance, which depends on the particle size, shape, and surrounding environment. When the size of gold nanoparticles is further reduced (<2 nm), they are known as gold nanoclusters or gold quantum dots (AuQDs), on which localized plasmons cannot be excited. Instead, due to the quantum confinement effect, electrons in AuQDs are excited from the ground state by absorbing near-UV light, and the AuQDs emit fluorescence in the visible range. The size of the

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† Electronic supplementary information (ESI) available: AFM images indicating the surface morphology of AuQD/PEDOT:PSS and AuQD/PEDOT:PSS/P3HT:PCBM films. *J-V* characteristics of the AuQD-loaded OSCs and AuQD/plasmonic AuNP OSCs. Summaries of photovoltaic parameters for the optimization of AuQD contents in the OSCs and the average carrier lifetimes. See DOI: 10.1039/c8na00119g



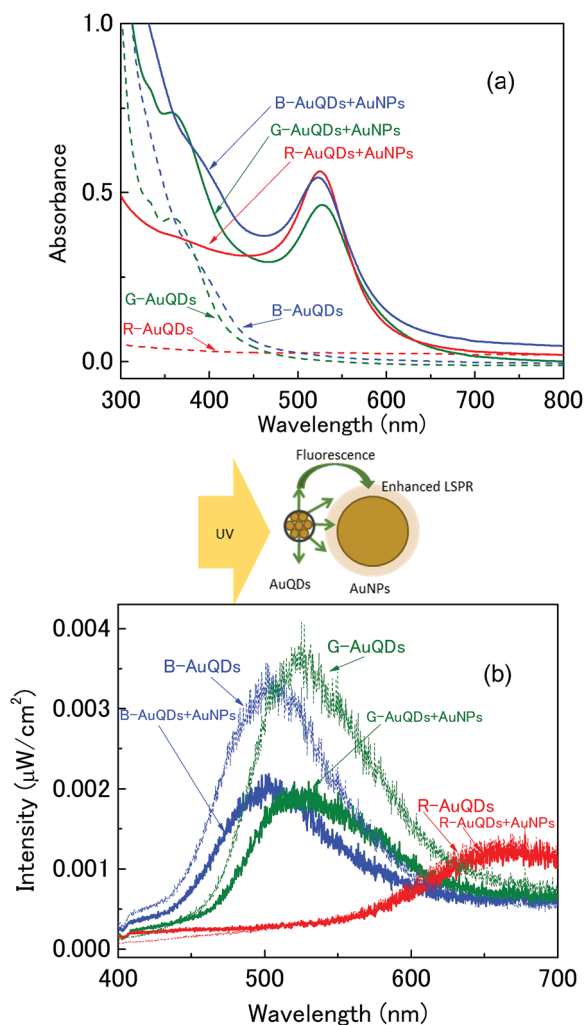


Fig. 1 (a) UV-vis absorption spectra and (b) fluorescence spectra of AuQDs and AuQD:AuNP aqueous solution.

The absorption spectra of the AuQD/AuNP complex exhibit a localized plasmon peak at around 525 nm in addition to the absorption baseline of AuQDs. It should be noted that the fluorescence peaks of B-AuQDs and G-AuQDs decreased considerably when they were mixed with the AuNPs. This result clearly indicates that the fluorescence emission of AuQDs is quenched by AuNPs. Especially, significant quenching was observed in the G-AuQD/AuNP complex. Because the fluorescence peak of G-AuQDs and the localized plasmon peak overlap significantly, the quenching can be considered mainly as an energy transfer, which should enhance localized plasmon excitation.²⁴ This is expected to enhance photocarrier generation in the active layer when the G-AuQD/AuNP complex system is used in OSC devices. However, almost no fluorescence quenching was observed for R-AuQDs/AuNPs. This is reasonable because the overlap between the absorption of AuNPs and the fluorescence emission wavelength of R-AuQDs is very small, resulting in almost no energy transfer in this system.

The surface morphologies of the AuQDs and AuQD/AuNP:PEDOT:PSS films were studied using atomic force

microscopy (AFM). In this experiment, an aqueous solution of AuQDs was deposited on an ITO/glass substrate by spin-coating as shown in the ESI, Fig. S4.† The appearance of bright spots on the surface originated from the aggregation of AuQDs with a size of *ca.* 5 nm. Although aggregation of AuQDs was observed on the film surface, a photograph of AuQDs under UV irradiation indicated homogeneous fluorescence (see Fig. S3†), indicating that the non-aggregated AuQDs were uniformly deposited on the substrate together with the aggregated AuQDs. It should be noted that the aggregated AuQDs with a size of 5 nm are expected to exhibit a plasmonic-like effect because the size of Au becomes similar to that of plasmonic AuNPs.²⁵ AFM images of PEDOT:PSS films and AuNP:PEDOT:PSS films on AuQD layers are presented in the ESI, Fig. S5.† A similar surface morphology was observed after spin-coating a pristine PEDOT:PSS solution on top of all the AuQD layers (ESI, Fig. S5(a-d)†). In addition, no significant differences in the morphologies of AuNP:PEDOT:PSS films deposited on different AuQD films were observed, and the surfaces exhibited some aggregation of AuNPs with a size of *ca.* 10 nm (ESI, Fig. S5(e-h)†). Because a large degree of aggregation or surface roughness at the interface of the PEDOT:PSS/P3HT:PCBM layer decreases the device performance, we optimized the concentration of AuNPs at 0.1 mM by measuring the OSC efficiency and the AFM morphologies.

Photovoltaic performance of AuQD/plasmonic AuNP solar cells

The proposed device structure of the AuQD/plasmonic AuNP solar cells consists of Al/P3HT:PCBM/PEDOT:PSS:AuNP/AuQD/ITO glass substrate as shown in Fig. 2(a). AuQDs emitting

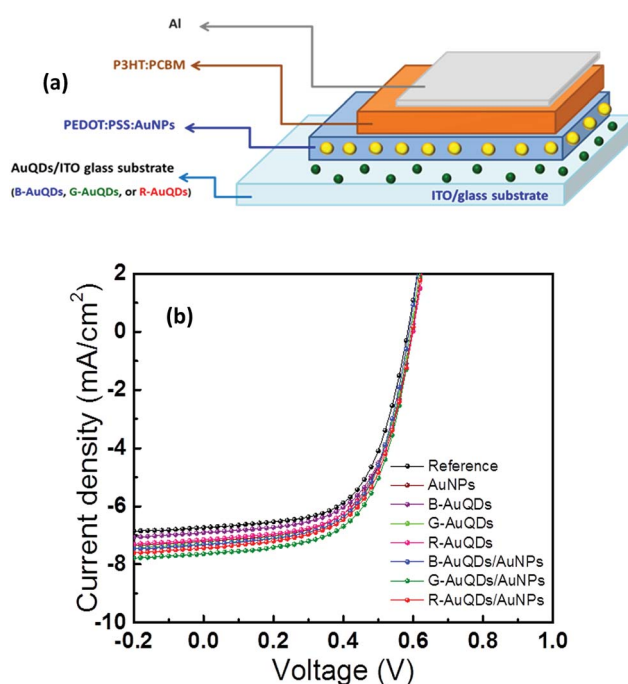


Fig. 2 (a) Schematic of the fabricated OSCs and (b) *J*-*V* characteristics of the OSCs compared with that of the reference cell.



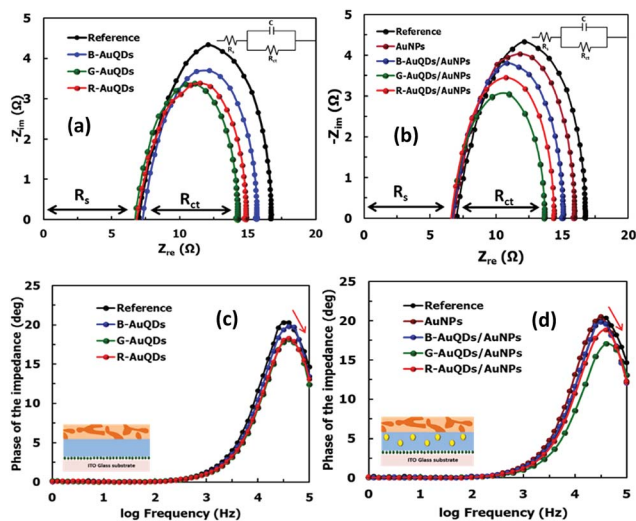


Fig. 4 Nyquist plots of the OSCs based on (a) individual AuQD layers and (b) the AuQD/plasmonic AuNP systems under solar light illumination. Bode phase plots of the OSCs based on (c) individual AuQD layers and (d) the AuQD/plasmonic AuNP systems under solar light illumination.

AuNP:PEDOT:PSS layers. On the other hand, the constant phase element in parallel with the charge transfer resistance (R_{ct}) corresponds to the capacitance, which is used to describe the distribution of carrier relaxation time at the active layer.³⁶ The R_{ct} values of the fabricated plasmonic solar cells decreased as a result of incorporation of the plasmonic layers. The R_{ct} values of the devices were derived as follows: 9.8 Ω for the cells with no plasmonic nanoparticles, 8.9 Ω for those with a AuNP:PEDOT:PSS layer only, 8.3 Ω for those with a B-AuQD layer only, 7.9 Ω for those with a R-AuQD layer only, and 7.3 Ω for those with a G-AuQD layer only. Interestingly, incorporating both AuNP:PEDOT:PSS and AuQD layers into OSCs resulted in lower R_{ct} values compared to those of individual systems, which were 8.1, 7.4, and 6.7 Ω for AuNP:PEDOT:PSS with B-AuQD, R-AuQD, and G-AuQD systems, respectively. This indicates that introducing AuNPs into the hole-transport layer (HTL) and a layer of AuQDs into OSCs could enhance the charge transfer.³⁰ Adding a AuQD layer could increase the number of photocarriers in the device *via* its fluorescence properties, which is consistent with the results obtained from $J-V$ measurements. These photo-generated carriers in the P3HT:PCBM layer should result from the absorption of UV and visible light fluorescence emission in the AuQD layer. Furthermore, the combination of AuQDs and AuNPs further increased the photocarriers. This could be due to an enhanced localized plasmon field at the AuNPs caused by the fluorescence emission of AuQDs and energy/electron transfer from the AuQDs to AuNPs, which corresponded to the fluorescence quenching shown in Fig. 1. Frequency peaks of the Bode phase plots for AuQD- and AuQD/plasmonic AuNP-OSCs are shown in Fig. 4(c) and (d), respectively. The frequency peaks are related to the electron lifetime in the devices.^{9,34,37} It could be seen that after adding a AuQD layer to the devices, the frequency peaks slightly shifted to higher frequency in comparison with that of the reference cell. Similarly, the OSCs with

AuQD/plasmonic AuNP systems exhibited higher frequency peaks compared to that of a cell with only AuNPs. The average electron lifetimes in organic solar cells can be investigated using impedance spectroscopy.^{36,38} The characteristic frequency peak of each OSC in Bode phase plots was employed to calculate the average electron lifetime (τ_{avg}).^{15,39} The average carrier lifetimes are summarized in Table S21 (ESI).[†] The results are not significantly different, suggesting that AuNP:PEDOT:PSS and/or AuQD layers might not significantly affect the carrier lifetime. Therefore, modification of the OSC configurations with the AuQD/AuNP complex improved the device performance mainly by the enhanced photocarrier generation due to the synergistic effect of fluorescence emission and enhanced plasmonic properties *via* energy/electron transfer from AuQDs to AuNPs.

Conclusions

We successfully designed an efficient AuQD/plasmonic AuNP system to manage light harvesting to enhance OSCs. A AuQD layer with green fluorescence emission and a AuNP:PEDOT:PSS HTL with localized plasmon excitation achieved the best light harvesting in OSCs. A G-AuQD/AuNP complex system exhibited enhanced photovoltaic performance (a J_{sc} of 7.61 mA cm⁻² and a PCE of up to 3.66% (13% improvement)), compared to reference OSCs. AuQDs could broaden light harvesting in the UV region and emit light in the visible region, which could be absorbed by the active layer as well as inducing energy/electron transfer to the plasmonic AuNPs, resulting in increased light harvesting in OSCs. Hence, the AuQD/AuNP complex system designed for OSCs has the potential to synergistically enhance OSC performance. Our strategy for light manipulation in OSCs using AuQDs and AuNPs is promising and could be applied to the development of other types of solar cells.

Conflicts of interest

There are no conflicts to declare.

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