Dependence of organic photovoltaic cell efficiency on the photoluminescence wavelength of core/shell quantum dots

Yensil Park [a], Kyoung Soon Choi [a], Heesun Yang [b], Soo Young Kim [a,*]

[a] School of Chemical Engineering and Materials Science, Chung-Ang University, 221 Heukseok-dong, Dongjak-gu, Seoul, 156-756, Korea
[b] Department of Materials Science and Engineering, Hongik University, Seoul, 121-791, Korea

ABSTRACT

We report on the effect of ZnCdS/ZnS and ZnCdSe/ZnS core/shell quantum dots (QDs) on the efficiency of organic photovoltaic (OPV) cells. The QDs were deposited on the back side of indium tin oxide/glass substrates by spin coating with poly (methyl methacrylate). The short circuit current (J_{SC}) and power conversion efficiency (PCE) of the OPV cells with ZnCdS/ZnS QDs + poly(methyl methacrylate) (PMMA) (8.07 mA/cm^2 and 3.2%) are higher than those of the control device without QDs (7.68 mA/cm^2 and 3.0%) because the wavelength of the injected light is changed to the absorption wavelength of the active layer of the OPV cells. However, the J_{SC} and PCE of the OPV cells with ZnCdSe/ZnS QDs + PMMA are lower than those of the control device (6.62 mA/cm^2 and 2.44%) due to the low transmittance of the QDs + PMMA and discordance between the emission peak of the QDs and absorption peak of the active area in the OPV cells.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Organic photovoltaics (OPVs) have gained much attention as one of the promising candidates for the generation of clean electricity, due to their light weight, flexibility, low cost, and high throughput fabrication methods [1,2]. Particularly, OPVs with a bulk heterojunction structure based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have been intensively investigated and found to have a power conversion efficiency (PCE) close to 4.4% [3].

In recent years, new device structures and novel active layer materials based on low band-gap polymers have been developed to further enhance the performance of OPVs [4–6]. Another method involves organic/inorganic hybrid solar cells using P3HT as an organic electron donor material and inorganic semiconductors of different kinds and shapes, for instance CdS, CdSe, PbS, PbSe, CuInS$_2$, and CdSe hyperbranched shapes, as an electron acceptor with efficient charge generation and charge transport [7–13]. However, their device efficiency is reported to be very poor compared to that of OPV cells using PCBM as an electron acceptor.

Colloidal semiconductor quantum dots (QDs) have novel optical and electrical properties resulting from their three-dimensional confinement. By combining different-sized QDs in one solar cell, more light can be absorbed and, therefore, more power delivered at greater efficiencies compared with solar cells made of bulk semiconductors. ZnS, CdS, ZnSe, and CdSe are semiconductors with bulk band gaps of 3.64,

2.42, 2.8, and 1.7 eV, respectively [14–17]. Therefore, ZnCdS/ZnS and ZnCdSe/ZnS core/shell QDs can be classified as Type-I. In this kind of core/shell heterostructured QDs, the valence band in the core is higher than that in the shell, but the conduction band in the core is lower than that in the shell. It has been reported that Type-I QD energy alignments produce a quantum well usually favoring exciton recombination and luminescence rather than dissociation [18]. As a result, QDs can be used to increase the emission efficiency at a specific wavelength. In our previous report, ZnCdSe/ZnSe QDs were used in OPV cells, but the device performance was degraded due to the low transmittance of the QDs and discordance between the emission peak of the QDs and absorption peak of the active area in the OPV cells [19]. It is expected that the efficiency of the OPV cells would be enhanced if the wavelength of the light emitted from the QDs were to match the absorption wavelength of the active layer in the OPV cells.

In this study, poly(methyl methacrylate) (PMMA), in which ZnCdS/ZnS core/shell QDs or ZnCdSe/ZnS core/shell QDs were embedded, was used to enhance the absorbance of light and, thereby, deliver power at greater efficiencies, as shown in Fig. 1. In order to attach QDs on the opposite side of an indium tin oxide (ITO)/glass substrate, a PMMA layer was used as a supporting material. According to their band gap energies, ZnCdS/ZnS and ZnCdSe/ZnS QDs emit blue and green light, respectively. The active layer of the OPV cells was composed of a blend of P3HT and PCBM. Thus, the ZnCdS/ZnS or ZnCdSe/ZnS QDs + PMMA would increase the light intensity in the blue region or green region, respectively, so that more light in this region would be absorbed by the OPV cells, thereby enhancing their efficiency. Therefore, the effects of the QDs + PMMA on the performance of the OPV cells are discussed. Furthermore, the dependence of the efficiency of the OPV cell on the photoluminescence

* Corresponding author. Tel.: +82 28205875.
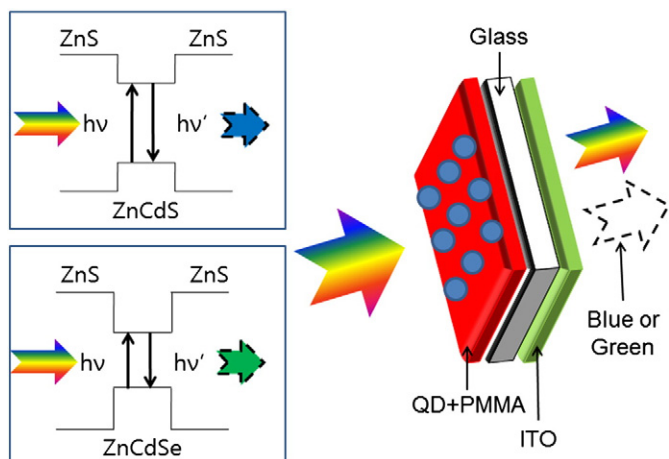 *E-mail address:* sooyoungkim@cau.ac.kr (S.Y. Kim).

Fig. 1. Schematic showing the mechanisms underlying the alteration of the wavelength of light of the OPV cell with QDs + PMMA film. The QDs are ZnCdS/ZnS and ZnCdSe/ZnS in this experiment.

(PL) wavelength of the core/shell QDs is discussed by comparing the two types of QDs.

2. Experimental details

In a typical synthesis of the green-emitting ZnCdSe QDs, 0.572 mmol of ZnO, 0.143 mmol of Cd acetate, 1 mL of oleic acid (OA), 0.7 mL of oleylamine (OLA), and 10 mL of 1-octadecene (ODE) were placed in a three-neck reaction flask. The mixture was heated to 170 °C with degassing. The flask was then purged with argon and its temperature was raised to 310 °C. At this temperature, a Se solution containing 2.316 mmol of Se powder in 1.2 mL of trioctylphosphine (TOP) was swiftly injected into the above hot mixture. The reaction mixture was maintained at 310 °C for 15 min for the growth of the QDs. The surface of the ZnCdSe core QDs was subsequently overcoated with a ZnS shell. A Zn stock solution was prepared by dissolving zinc acetate (2.86 mmol) in a mixture of OA (2 mL), OLA (2 mL), and ODE (1 mL) at 150 °C and a S stock solution by dissolving S (7.72 mmol) in TOP (4 mL) at the same temperature. For the coating of the ZnS shell, the crude solution of the ZnCdSe core QDs was cooled to 270 °C and the Zn stock solution was injected first, followed by the dropwise addition of the S stock solution. For the synthesis of the ZnCdS QDs, an S solution containing 0.286 mmol of S in 1 mL of ODE was injected into the hot mixture consisting of 0.286 mmol of ZnO, 0.143 mmol of CdO, 1 mL of OA, and 10 mL of ODE. The surface of ZnCdS core QDs was also capped with a ZnS shell using Zn and S stock solutions, where 1.716 mmol of Zn acetate and 1.144 mmol of S were dissolved in the same amounts of organic mixtures used for the preparation of the ZnCdSe core QDs. The experimental details for the growth of the ZnCdS core and subsequent ZnS shell overcoating were identical to those for the ZnCdSe/ZnS QDs. The as-grown ZnCdSe/ZnS and ZnCdS/ZnS QDs were purified 3 times with a combined hexane/methanol solvent and then dispersed in chlorobenzene.

A solution composed of 2 g of PMMA in 5 mL of chloroform was prepared and mixed with 2 mL of the QDs in chlorobenzene. Glass coated with ITO (150 nm thick, ~20 Ω/sq) was used as the starting substrate. The sol was coated on the back side of the ITO/glass substrate at a rate of 1000 rpm for 20 s. An ITO/glass substrate without QDs + PMMA films was also prepared for use as a reference. Active blend films were fabricated between a transparent ITO anode and a reflective cathode. The ITO surface was cleaned using UV-ozone treatment for 15 min prior to device fabrication. After the UV-ozone treatment, the substrates were transferred to a N$_2$-filled glove box. Poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) was spin-coated on top of the ITO anode in the OPV cells with P3HT (RIEKE METALS):PCBM (NANO-C, 99.5%) to act as

a hole extraction layer. P3HT was first dissolved in 1,2-dichlorobenzene to make a 20 mg/mL solution, followed by blending with PCBM at a weight ratio of 6:4. The blend was stirred for ~24 h in a glove box before being spin-coated on top of the ITO anode. The thickness of the active layer was measured to be ~200 nm by a surface profiler (Tencor Alphastep 500). The devices were annealed on a hot plate in a glove box at 110 °C for 10 min. The cathode was fabricated by depositing LiF (ca. 1 nm) and Al (ca. 100 nm) at a base pressure of 2×10^{-6} Torr. The active device area was ca. 0.04 cm^2. The current density–voltage (J–V) curves were measured under air ambient with glass encapsulation using a Keithley 2612A source measurement unit. The photocurrent was measured under AM1.5G 100 mWcm^{-2} illumination. The maximum PCE for the conversion of solar radiation to electrical power was calculated by the equation: $\frac{V_{oc} \times J_{sc} \times FF}{P_{in}(=100mW/cm^2)} \times 100$, where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, FF is the fill factor, and P_{in} is the illuminated power.

The absorption characteristics of the QDs and transmittance spectra were measured by UV–visible absorption spectroscopy (Shimadzu, UV-2450). The PL spectra of the QDs were collected by a spectrofluorometer (Jobin Yvon Inc., Fluorolog 3) equipped with a 450 W Xe lamp. The PL quantum yield of a diluted solution of the QDs with an optical density of ~0.05 was calculated by comparing their integrated emission with that from a Rhodamine 6G standard solution.

3. Results and discussion

Fig. 2 shows the excitonic absorption spectra and PL emission spectra of the ZnCdS/ZnS and ZnCdSe/ZnS QDs. The absorption peak intensity of the ZnCdS/ZnS QDs decreased with increasing wavelength. In the case of the ZnCdSe/ZnS QDs, the absorption peak intensity also decreased with increasing wavelength, but another excitonic absorption peak exhibited at 530 nm. The PL emission peaks were maximized at 448 nm and 543 nm for the ZnCdS/ZnS and ZnCdSe/ZnS QDs, respectively, which were red-shifted relative to their absorption peaks. The images of each QD are shown in the inset of Fig. 2. The PL quantum yields of the core/shell QDs were measured to be ~80% for ZnCdS/ZnS and ~55% for ZnCdSe/ZnS.

The UV–Vis absorption spectra of the P3HT:PCBM composite films with different amounts of PCBM without annealing are shown in Fig. 3(a). The absorption of the films decreased significantly with increasing amount of PCBM in the visible range, specifically between 450 and 600 nm, which is the peak absorption wavelength band for P3HT. The maximum absorption wavelength (λ_{max}) for the film with P3HT: PCBM = 4:6 was ~506 nm with shoulders at ~555 and ~610 nm. The λ_{max} for P3HT:PCBM = 5:5 was ~516 nm and that for P3HT:PCBM = 6:4 was ~at 517 nm, showing an increasing red-shift as the amount of P3HT increased. It has been reported that the peak shift comes from
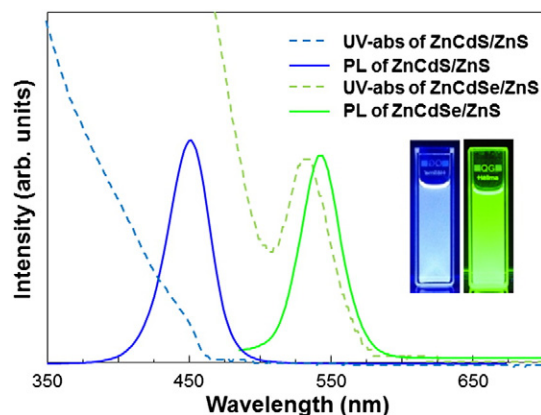

Fig. 2. UV–Vis absorption and PL emission spectra of ZnCdS/ZnS and ZnCdSe/ZnS QDs.