



Nanoscale photovoltaic characteristics of single quantum dot hybridized with poly(3-hexylthiophene)



Yoon Deok Han^a, Sumin Jeon^b, Sun Dal Kim^c, Ji-Hee Kim^d, Sang Youl Kim^c, Jeongyong Kim^d, Kwang-Sup Lee^{b,*}, Jinsoo Joo^{a,*}

^a Department of Physics, Korea University, Seoul 136-713, Republic of Korea

^b Department of Advanced Materials, Hannam University, Daejeon 305-811, Republic of Korea

^c Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea

^d Center for Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS); Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea

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ABSTRACT

Hybrids consisting of CdSe/ZnS quantum dot (QD) as a core and thiol-group functionalized poly(3-hexylthiophene) (P3HT) as a shell were fabricated using the ligand-exchange method. We clearly observed the photovoltaic characteristics of a single QD-P3HT hybrid by using conducting atomic force microscopy. Monochromatic power conversion efficiency drastically increased with an increase in the molecular weight (Mw) of P3HT, suggesting sufficient photoinduced charge transfer between the QD and highly ordered P3HT chains. The nanoscale photoluminescence (PL) intensity for a single QD considerably decreased with increasing Mw of P3HT owing to charge transfer effects. On the basis of time-resolved PL and transient absorption spectra measurements of the QD-P3HT hybrids, we deduced that the exciton lifetimes of the QD were reduced with higher-Mw P3HT hybrids, and photobleaching was observed. The measured nanoscale optical characteristics of the single QD-P3HT hybrids support their distinct photovoltaic behaviors.

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1. Introduction

Semiconducting CdSe quantum dots (QDs) show high quantum yield and tunable emission spectra due to quantum confinement effects [1–4]. Many efforts have been made to fabricate functional QDs using functionalized capping agents with high binding affinity for solution-based processes, the stabilization of the QDs, and their uniform dispersion in a solvent [5]. Using ligand exchange of the QDs, one can attach functional *p*-type organic molecules to the surface of QDs [6]. This hybridization leads to distinct luminescence and charge transport characteristics

resulting from energy/charge transfer effects [7]. The characteristics of the hybrids of QDs with π -conjugated molecules in bulk scale had been reported previously [8–10].

Photovoltaic devices have been studied intensively and fabricated with various combinations of *p*-type and *n*-type organic and/or inorganic materials [11–14]. Photovoltaic cells using CdSe nanorods mixed with regioregular poly(3-hexylthiophene) (P3HT) showed 1.7% power conversion efficiency (PCE) at AM 1.5 [15]. The use of colloidal QDs in photovoltaic devices contributed to the enhanced PCE and simplified the fabrication. For example, a PCE of up to 6% in colloidal PbS QD-based photovoltaic devices has been achieved at AM 1.5 [16]. Hybrids with molecular hetero-junctions between QDs and organic molecules, showing improved charge transfer efficiency, hold promise both as active materials for photovoltaic devices and as

* Corresponding authors. Tel.: +82 42 629 8857; fax: +82 42 626 8854 (K.-S. Lee). Tel.: +82 2 3290 3103; fax: +82 2 927 3292 (J. Joo).

E-mail addresses: kslee@hnu.kr (K.-S. Lee), jjoo@korea.ac.kr (J. Joo).

novel building blocks for future nanoscale photovoltaic devices [17,18]. The degree of the spectral overlap and the physical distance between the two *n*-type and *p*-type species play important roles in enhancing the photovoltaic characteristics through the charge transfer phenomena. Considering these points, we designed and synthesized molecular junction hybrids consisting of a CdSe/ZnS QD as a core and *p*-type P3HT molecules with varying molecular weight ($M_w = 3000, 6000, \text{ and } 10,000$) as a shell (hereafter “QD-P3HT hybrid”) using the ligand-exchange method.

In this study, the nanoscale optical and photovoltaic current–voltage (*I*–*V*) characteristics were investigated for a single QD-P3HT hybrid with different molecular weights (M_w s) of P3HT. The laser confocal microscope (LCM) photoluminescence (PL) intensity of a single QD drastically decreased after attaching the P3HT to the surface owing to the charge transfer effect between the QD and *p*-type P3HT. In the single QD-P3HT hybrids, the charge transfer rates between the QD and P3HT were observed to depend on the M_w of P3HT. These results were confirmed by the variation of the QD exciton lifetimes determined using time-resolved PL decay curves and transient absorption spectra. On the basis of the photovoltaic *I*–*V* characteristics investigated through conducting atomic force microscope (CAFM) experiments under a 488 nm monochromatic source, the PCE (η) of a single QD-P3HT hybrid was enhanced from 0.10% to 0.22% with an increase in the M_w of P3HT from 3000 to 10,000. The results can be analyzed in terms of the increase in photoinduced charge transfer efficiency between the QD and P3HT when P3HT of high M_w with highly ordered main chains was hybridized.

2. Materials and methods

2.1. Fabrication of QD-P3HT hybrids

Allyl-terminated regioregular poly(3-hexylthiophene) (allyl-P3HT) was synthesized via the Grignard metathesis reaction [19,20]. The M_w s of the polymers were controlled by regulating the Ni(dppp)Cl₂ concentration with a constant monomer concentration [21,22]. 2,5-Dibromo-3-hexylthiophene (3.26 g, 10 mmol) was dissolved in 100 mL of tetrahydrofuran (THF) and stirred under N₂ gas. A 2 M solution of *tert*-butylmagnesium chloride in diethyl ether (5.0 mL, 10 mmol) was added using a gas-tight syringe, and the mixture was gently refluxed for 2 h. The oil bath was then removed, and the reaction mixture was allowed to cool to 23–25 °C, after which Ni(dppp)Cl₂ (0.55, 0.37, 0.19 mmol) was added as a suspension in anhydrous THF. With decreasing Ni(dppp)Cl₂ concentration, the M_w of allyl-P3HT increased to 3000 ($M_w = 2.9 \times 10^3$, PDI = 1.14), 6000 ($M_w = 6.6 \times 10^3$, PDI = 1.08), and 10,000 ($M_w = 9.8 \times 10^3$, PDI = 1.11) Da, respectively (Fig. S1 in Supplementary Content). The mixture was stirred for 15 min at room temperature (RT), and 1 M solution of allylmagnesium bromide in diethyl ether (4.5 mL, 4.5 mmol) was added to it using a syringe. The mixture was stirred for an additional 5 min and then poured into

methanol to precipitate the polymer. The polymer was filtered into an extraction thimble and then washed by Soxhlet extraction with methanol, hexanes, and chloroform. The polymer was then isolated from the chloroform extraction.

2,2-Dimethoxy-2-phenylacetophenone (DMPA) and thiol compound (ethanedithiol) were purchased from Sigma Aldrich and used without further purification. The thiol-ene click reaction was adapted for the preparation of thiol-terminated P3HT [23]. Allyl-terminated P3HT (0.08 g), 1,2-ethanedithiol (0.8 mL, 9.5 mmol), and 2,2-dimethoxy-2-phenylacetophenone (0.0266 g, 0.10 mmol) were dissolved in 8 mL THF in a Schlenk flask. The flask was then degassed over three freeze-pump-thaw cycles and stirred under irradiation with 365 nm light (Vilber Lourmat VL-4 LC) for 4 h at RT. The light power was 4 W. The reaction mixture was then precipitated in methanol, [22] and quantitative induction of the allyl end group into thiol functional group was confirmed by ¹H NMR and MALDI-TOF spectroscopic technics (Figs. S2 and S3). The oleic-acid-stabilized CdSe/ZnS QDs (5 mg) and thiol-terminated P3HT (50 mg) were dispersed in chloroform (5 mL) and ethanol (5 mL) under sonication for 3 h. Chloroform (40 mL) was then added into the mixture to precipitate the 11-mercapto-1-undecanol-capped CdSe/ZnS QD. Fig. 1a shows a schematic of the chemical structure of thiol-functionalized P3HT. Fig. 1b shows the schematic illustration of a single QD-P3HT hybrid. Fig. 1c shows a schematic of the synthetic procedure of the QD-P3HT hybrid using thiol-functionalized P3HT and the ligand-exchange method [24].

2.2. Measurements

The formation and surface morphologies of the core-shell type QD-P3HT hybrids were investigated using a field-emission transmission-electron microscope (FE-TEM, Tecnai 20, FEI, USA). The ultraviolet and visible (UV-Vis) absorption spectra of the QD-P3HT hybrids in chloroform solution were measured using an Agilent 8453 spectrometer. The X-ray diffraction (XRD) patterns of P3HT were measured using an X-ray diffractometer (Rigaku Model D, Japan; $\lambda = 1.54 \text{ \AA}$). The transient absorption (TA) spectra of the samples were measured using a Coherent Libra Series, TOPAS prime (Coherent, USA) as a light source and a TA spectrometer (HELIOS, Ultrafast Systems, USA). The Fourier-transform infrared (FT-IR) spectra of the samples were measured using an FT-IR Series spectrometer (Infinity gold, ThermoMattson, USA). For FT-IR measurements, the samples were homogeneously mixed with KBr and then dried. The solution PL spectrum of the green QDs in chloroform solution was measured using fluorescence spectrophotometers (F-7000, Hitachi, Japan). For measuring the nanoscale solid-state luminescence characteristics, the QDs and the QD-P3HT hybrids were drop-cast onto a glass cover slip, after which the PL spectra of the single hybrids were measured using a homemade LCM (Monochromator: Acton spectra Pro 300i, CCD: Acton PIXIS 100, scan stage: PSIA XE-120) with fine spatial resolution (about 200 nm). A laser with an excitation wavelength of 405 nm was used in the LCM PL measurement system. The excitation power and acquisition time for the LCM PL mapping images were fixed

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