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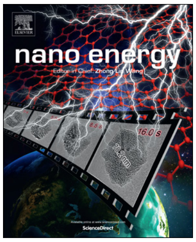

RAPID COMMUNICATION

Silicon nanocrystal conjugated polymer hybrid solar cells with improved performance

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Abstract
Hybrid inorganic/organic solar cells based on silicon nanocrystals (NCs) and conjugated polymers are optimized through tuning the surface termination of Si NCs and selecting a narrow bandgap conjugated polymer. Here freestanding Si NCs are blended with either P3HT or PTB7 in a solution phase. The resulting mixture is spin-cast to form a bulk hetrojunction structure, on which a hybrid solar cell is fabricated. It is found that by altering the surface termination of Si NCs from predominately chlorine termination to hydrogen termination the power conversion efficiency (PCE) of a hybrid solar cell is significantly improved. PTB7-based solar cells efficiently respond to a wider spectrum of sunlight than P3HT-based ones. This is due to the lower bandgap of PTB7 compared to P3HT (~1.8 eV vs. ~2.0 eV). Finally, PCE up to 2.2% has been achieved in solar cell fabricated by using hydrogen-terminated Si NCs and PTB7.

Introduction

Organic photovoltaics (OPVs) have attracted much attention in recent years due to the potential for solution-based roll-to-roll production of cost-effective flexible solar cells over a large area [1-5]. Recently several groups have surpassed 10% power conversion efficiency (PCE), a significant milestone to commercialization [6-8]. Despite the remarkable success in improving PCE, other factors besides PCE are also important for commercialization such as, cost, processability, environmental concerns, and service life [9]. Hybrid solar cells (HSCs) offer an alternative approach by replacing the electron acceptor

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material (generally fullerenes) with an inorganic semiconductor, whilst retaining the advantages of organic materials, especially in terms of their ability to form films by solution process [10]. In addition, inorganic semiconductor nanocrystals (NCs) have highly desirable properties such as size-dependent optical and electronic properties [11], multiple exciton generation (MEG) [12,13], and control of carrier concentration and type through doping [14,15].

To date, hybrid solar cells with various NCs of different shapes and materials have been fabricated [16]. Among them, CdS and PbS_xSe_{x-1} quantum dot-based HSCs demonstrate remarkable PCE of 4.1% and 5.5%, respectively [17,18]. However, toxicity of these materials is prohibitive to vast commercial application. Employing wide bandgap metal-oxide NCs such as TiO_2 and ZnO alleviates the concerns of toxicity and PCE as high as 2% have been demonstrated [19-21]. However, these wide bandgap materials do not assist in significant energy conversion through absorption and their role is limited to dissociation of excitons and transport of carriers. Therefore a material that is environmentally friendly and is an active absorber is desirable.

Silicon nanocrystals (Si NCs) are environmentally benign and with a bulk bandgap of 1.1 eV offer the possibility to assist in light absorption, especially towards the UV [22-24]. Mass production can be realized by means of nonthermal plasmas [25,26]. Si NC-based HSCs with PCE about 1% have already been achieved by several groups in 2010 [27-29]. We intend to combine the advantages associated with both conjugated polymers and Si NCs to fabricate high efficiency HSCs. In this work, we demonstrate that the PCE of Si NC-based HSCs can be improved by a factor of three through NC surface modification. In addition, by utilizing a low bandgap polymer, a PCE of 2.2% is achieved, which is the highest value that has been reported for Si NC-based device.

Experimental section

Nanocrystal fabrication

Si NCs were synthesized by using a nonthermal plasma process as previously described elsewhere [25,30]. A quartz tube with inner diameter of 45 mm was employed as the reactor. Very high frequency (VHF) at 70 MHz was supplied on two copper electrodes surrounding on quartz tube. All Si NCs were synthesized with 8 standard cubic centimeters per minute (sccm) of silicon tetrachloride ($SiCl_4$), 80 sccm of H_2, and 240 sccm of Ar at a pressure of 400 Pa with an applied power of 65 W. Si NCs synthesized in the plasma were collected downstream of the plasma on a stainless mesh. All of the synthesis and handling of Si NCs was conducted without exposure to air unless otherwise noted. These conditions result in Si NCs with narrow size distribution (a standard deviation of $<20\%$) that are freestanding and have an average size about 6 nm as shown in typical AFM and TEM images in Figure S1 (see Supporting information).

Surface component modification

Si NCs were exposed in air for 30 min to remove surface chlorine. Hydrofluoric acid (HF) etching was performed using a Teflon supporting mesh for the Si NC powder and put above a 50% HF water solution in a sealed container at room temperature for the specified times. After etching Si NCs were collected in a vial and returned immediately to a glovebox. Solutions of 30 mg/mL were prepared with 1, 2-dichlorobenzene (DCB, anhydrous, Sigma Aldrich) and chlorobenzene (CB, anhydrous, Sigma Aldrich) as solvent for Si NC/poly(3-hexylthiophene-2,5-diyl) (regioregular P3HT, Sigma Aldrich, extinction coefficient at 520 nm = ~0.6 [31]) and Si NC/poly[[4,8-bis[(2-ethylhexyl) oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]-thieno[3,4-b]thiophenediyl]] (PTB7, Sigma Aldrich, extinction coefficient at 670 nm = ~0.6 [6]) device, respectively.

Characterization

Atomic force microscopy (AFM) images were obtained by spin-casting Si NCs on a cleaned silicon substrate and measuring with a scanning probe microscope (SHIMADZU, SPM-9600). Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010F transmission electron microscope. Absorption spectra were recorded by depositing respective films on corning glass (JASCO V-550). FTIR spectra were taken by depositing Si NCs directly on one window of air-free thallium bromoiodide (KRS-5) cell and corresponding spectra were recorded in transmission mode with a resolution of 4 cm^{-1} (JASCO FT/IR-6100).

Device fabrication and testing

Device fabrication and measurements were all performed in a nitrogen-purged glovebox (<1 ppm water and oxygen). Commercially available ITO glass with sheet resistance of 15 Ω/□ and thickness of 250 nm was employed as the substrate. The ITO was patterned with photolithography and wet etching was used to define the electrodes. (poly (3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid)) (PEDOT:PSS, CLEVIOS PH 1000, Heraeus) mixed with 5 wt% of dimethyl sulfoxide (DMSO, Sigma Aldrich) and 0.1 wt% of Zonyl (FS-300, Sigma Aldrich) was spin cast on it at 4000 rpm for 1 min and annealed at 130 °C for 5 min [32,33]. Si NC/polymer blend solutions were stirred for 24 h prior to use and spin cast at 1200 rpm. Finally, Al electrode with thickness of 100 nm was evaporated through a shadow mask (active area 4.6 mm^2). 6 devices were prepared to obtain the standard deviations. Devices were annealed at 110 °C for 2 h before characterization. Photocurrent density-voltage (*J-V*) curves were measured under 1 sun illumination with a Keithley 2400 Digital Source Meter. Light source was calibrated by Asahi Spectra Co., Ltd. Incident light power is checked before every measurement by using a standard silicon photodiode. Devices were also encapsulated to confirm *J-V* and external quantum efficiency (EQE) spectra were also measured on a Hypermonolight system in open air (Bunkoukeiki, CEP-25BX). Encapsulation avoids detrimental influence from oxygen and moisture. Photo of device before and after encapsulation can be found in Figure S2 (see Supporting information).