



Modeling of optimum size and shape for high photovoltaic performance of poly(3-hexylthiophene) nanopore in interdigitated bilayer organic solar cells



Jae-hyeong Lee ^{a, *}, Takashi Sagawa ^b, Makoto Takafuji ^{a, c}, Hirotaka Ihara ^{a, c}

^a Department of Applied Chemistry and Biochemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555, Japan

^b Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

^c Kumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Kumamoto, 862-0901, Japan

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ABSTRACT

The interdigitated design for donor–acceptor in solar cell has been studied in some detail, but the optimum size and shape leading to direct enhancement in nanopore (or nanopillar) structure is still not well understood. Here, we demonstrate a modeling method to forecast the optimum size and shape for poly(3-hexylthiophene) (P3HT) nanopores in interdigitated P3HT: [6, 6]-phenyl C₆₁ butyric acid methyl ester (PCBM) photovoltaic device, based on experimental results of P3HT:PCBM bilayer solar cell. In our analysis, the energy generated at unit nanopore is supposed to be the same as the one generated at infinite point of P3HT:PCBM bilayer solar cell with variable layer thickness. A definitive function in terms of a radius of unit nanopore with various shapes is established, substituting a regression function derived from the results of power conversion efficiency in bilayer solar cell. Interpreting the function, we finally showed that the effective radius for P3HT nanopores with rectangular or cylinder, cut-cone, cone shape should be less than 135, 53, 2 nm respectively.

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1. Introduction

Ordered and interdigitated structure, based on vertically well-aligned conjugated polymer nanorods surrounded by the acceptor material to realize bicontinuous heterojunction morphology, has been considered as the ideal structure for the active layer. Interfacial area in ordered structure, which is substantial to generate charges dissociation within the exciton diffusion length (EDL) (~10 nm) [1–3], is enlarged as much as bulk heterojunction (BHJ) structure devices, while continuous pathways for the dissociated charges to reach to the respective electrodes increase. To obtain nanostructured-conjugated polymer such as P3HT, nanoimprint lithography using a Si mold [4–6] and anodic aluminum oxide (AAO) templates [7–14] as an inexpensive method for polymer-based nanostructures has been developed intensively. Recently, several groups have proposed a novel idea of developing phase segregation between two polymers and removing the sacrificed polymer in subsequent step [15–20]. We have also

reported perpendicularly phase separated nanopillar structure using self-assembling low molecular weight organic compound [21].

The height and size of nanopore are significant factors to decide how much the nanopores contribute to enhancement for PCE (Power Conversion Efficiency). The height of nanopore would be generally controlled close to the total thickness of active layer, even though the fabrication is somewhat difficult. In order to enlarge interfacial area, it is clear that we induce the development for smaller nanopore if possible. However, too small nanopores would be damaged by the coating process of top layer, which is coated on nanopores in sequential coating for bilayer. Further, the narrow width of nanopores prevents the solution for top layer inserting into the nanopore between nanorods. Accordingly, we should attempt to trade off between process manipulation and size control through its individual manner. Meanwhile, previously reported researches have been focused on how to make nanopores smaller, regardless of three-dimensional structures for nanopore. However, it is required to be selected an optimum template or mold which decides the shape of nanopore in pressure-type method such as nanoimprint lithography and AAO membranes. In chemical reaction method such as phase segregation and removal, it would be harder to control the shape of nanopore. If we can predict the

* Corresponding author.

E-mail address: leemin@kumamoto-u.ac.jp (J.-h. Lee).

optimal shape of the nanopore, further manipulations such as controlling the concentration, the reaction rate and the pre-post treatment can be implemented for the specific shape. Despite these necessities, any of experimental and theoretical studies for optimization of the size and the shape in P3HT nanopore have not yet been investigated to the best of our knowledge.

We hereby demonstrate a modeling analysis to decide size and shape for most effective P3HT nanopores, suggesting the analogy between bilayer and nanopore structures in terms of energy generation. A regression function for PCEs as to height of nanopore is derived from experimental results of bilayer solar cells with the thickness of 20/80, 40/60, 60/40, and 80/20 nm in P3HT:PCBM. We set up an inequation using the function and the integration, satisfying a requirement that amount of energy generated in flank and bottom sides of unit nanopore is greater than the one obtained at interface of bilayer solar cell. Accordingly, we obtain an optimum and maximum radius for nanopores with various shapes, depicting a final function via this inequation.

2. Experimental section

In the preparation of solar cell devices, indium-tin-oxide (ITO) coated glass substrates ($5 \Omega \text{ cm}^{-2}$) were first patterned by etching and then cleaned thoroughly with a sequence of solvents: detergent, deionized water, acetone and isopropanol, for 10 min each in an ultrasonic bath. The cleaned substrates were purified further by oxygen plasma treatment for 10 min. The substrates were then spin coated with a $0.45 \mu\text{m}$ filtered poly (3, 4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) solution (Clevios P), purchased from HC Starck, at 4000 rpm for 60 s to produce a 40 nm thick layer. The substrates were subsequently heated on a hotplate in air at 200°C for 10 min to remove excess water. For the thickness studies, we prepared solutions of P3HT (Rieke Metals) in *o*-dichlorobenzene at concentrations of 5, 10, 15, 20 mg/mL. After the solutions dissolve in ultrasonic bath at 50°C , these solutions were spin coated onto the PEDOT:PSS coated substrates at 1000 or 2000 rpm for 30, 35, 45, 65, 85, 90 s. P3HT films were allowed to dry in a N_2 atmosphere for at least 10 min before thickness measurement. To obtain accurate values for thickness of PCBM, we spin coated PCBM solutions onto P3HT layers, not a ITO coated glass or a PEDOT:PSS layer. For coating of the PCBM layer, we prepared solutions of PCBM in DCM at concentrations of 3, 7.5, 10 mg/mL. The thickness of PCBM layers was controlled by rotation speed of 1500, 1800 and 2000 rpm, fixing a rotation time of 10 s. Preparation for fabrication of P3HT:PCBM bilayer solar devices was basically similar to the preparation for measurement of thickness of P3HT or PCBM. After coating process for active layer, the titanium tetraisopropoxide in ethanol ($10 \mu\text{L}/3 \text{ mL}$) solution was at 4000 rpm spin-cast in air on top of the PCBM layer. Subsequently, during 0.5 h in air at room temperature, the precursor converted to TiO_x by hydrolysis. Subsequently the device was pumped down in vacuum ($5 \times 10^{-3} \text{ Pa}$), and a $\sim 100 \text{ nm}$ thick Al electrode was deposited by thermal evaporation. The photovoltaic characteristics were measured under nitrogen atmosphere using an Agilent 4156C parameter analyzer under AM1.5 (100 mW cm^{-2}) simulated illumination using a solar simulator with a 1000 W xenon arc lamp.

3. Results and discussion

3.1. Analogy between nanopore and bilayer in terms of generating energy

Considering the structure and origin of nanopores, we notice that the formation of nanopore is similar to a process that an interfacial side (upper side in nanopore) in bilayer changes into a

cylinder shape with a flank and bottom side, as shown in Fig. 1a. Accordingly, when we need to confirm any quantitative change in the process of developing nanopores, it is reasonable that generated energy at interfacial side of bilayer is compared to the produced energy at flank and bottom side of a unit nanopore. We assume that the PCE only depends on a newly developed nanopore, regardless of the number of nanopores and the area of unchanged interface. For this purpose, we apply a notion of generated energy, which is used as a calculation tool for solar energy in a large module. The generated energy (Q) in the photovoltaic system is given by

$$Q \propto P \cdot A, \quad (1)$$

where P is a PCE in unit device and A is a unit area. When the value of P and A can be obtained as a function of the height of nanopore (h) and the radius (r) respectively, the generated energy (Q) in a solar cell with nanopore is expressed below;

$$Q(h, r) = P(h) \cdot A(r). \quad (2)$$

To induce any enhancement in PCE via these nanopores, we should design and develop the structure of nanopores, in which the amount of energy generated in flank and bottom sides is greater than the one obtained in the original interface. The conditions lead to an inequation given by

$$Q_S < Q_F + Q_B, \quad (3)$$

where Q_S , Q_F and Q_B are the sum of energy obtained at surface, flank and bottom side respectively.

Fig. 1b shows the illustration of nanopores, so-called ideal types in P3HT:PCBM active layer. The size (diameter and height) and shape of nanopores depend on the fabrication process of these nanostructures. Nanoimprint lithography and AAO templates produce more regular and stable nanostructure including nanotubes, nanorods and nanopores, compared to ones obtained from chemical reaction by polymer templates [4–7,12,22–25]. In Fig. 1c, a cylindrical P3HT nanopore, which is surrounded by P3HT nanopillars, is covered with PCBM as a typical shape. We focus on the transportation of electrons (black dot and upward arrow) and holes (white dot and downward arrow) toward each anode and cathode along a cylindrical nanopore. Supposing that an electron and a hole generated at certain point of cylindrical nanopore move to each electrode without any obstruction, a PCE at the point can be represented by a PCE obtained at P3HT:PCBM bilayer films with each thickness as shown in Fig. 1c and d. For example, the shortest path of an electron and a hole at S_3 (the point of one-third of total nanopore) in Fig. 1c corresponds to the thickness of P3HT layer (60 nm) and PCBM layer (40 nm) in Fig. 1d, respectively. Note that this assumption is valid only if no delay in carrier transportation on the way to the electrode happens despite of increased carriers in nanopore structure. Consequently, experimental PCEs of P3HT:PCBM bilayers with various thickness combinations allow us to predict a PCE (P_h) at certain height (or depth) of nanopore.

Fig. 2 shows the structure and planer illustration of several representative nanopores with rectangular, cylinder, cut-cone and cone shape. We set that the radius of upside (the length of a half-side in rectangular) and the height of nanopore is r , h respectively. In cut-cone shape nanopore, the radius of bottom side ($r/2$) is selected as the intermediate value between the radius of cylinder (r) and cone (0). P_S and P_B represent PCEs at surface (or upside) and bottom side per unit area as shown in Fig. 2. Considering these planer illustrations in Fig. 2, the development of nanopore means obviously that a surface changes to multiple faces including flank

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