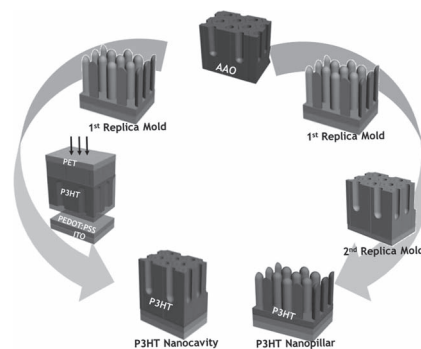


# Toward Mass Producing Ordered Bulk Heterojunction Organic Photovoltaic Devices

Taeyong Kim, Hyunsik Yoon, Hyung-Jun Song, Niko Haberkorn, Younghyun Cho, Seung Hyun Sung, Chang Hee Lee, Kookheon Char,\* Patrick Theato\*

A strategy to fabricate nanostructured poly(3-hexylthiophene) (P3HT) films for organic photovoltaic (OPV) cells by a direct transfer method from a reusable soft replica mold is presented. The flexible polyfluoropolyether (PFPE) replica mold allows low-pressure and low-temperature process condition for the successful transfer of nanostructured P3HT films onto PEDOT/PSS-coated ITO substrates. To reduce the fabrication cost of masters in large area, we employed well-ordered anodic aluminum oxide (AAO) as a template. Also, we provide a method to fabricate reversed nanostructures by exploiting the self-replication of replica molds. The concept of the transfer method in low temperature with a flexible and reusable replica mold obtained from an AAO template will be a firm foundation for a low-cost fabrication process of ordered OPVs.



## 1. Introduction

In recent years, different renewable energy sources are critically examined to solve the worldwide energy crisis for sustainable development, and photovoltaic devices are regarded as quite suitable candidates taking into account the almost infinite amount of solar energy available.

Organic photovoltaic (OPV) cells have currently received intense attention, because they combine many advantages, when compared with commercialized silicon solar cells, such as flexibility, cheap processing cost, and high absorption coefficient of organic films.<sup>[1–3]</sup> Today, it has been widely accepted that “ordered bulk heterojunction” (OBHJ) OPVs are a very promising solution to achieve

T. Kim,<sup>[†]</sup> Y. Cho, S. H. Sung, Prof. K. Char, Prof. P. Theato  
The National Creative Research Initiative Center for Intelligent Hybrids, The WCU Program of Chemical Convergence for Energy and Environment, School of Chemical and Biological Engineering, Seoul National University, Seoul, 151-744, Korea  
E-mail: khchar@plaza.snu.ac.kr

Prof. P. Theato  
Institute for Technical and Macromolecular Chemistry,  
University of Hamburg, Bundesstrasse 45, 20146 Hamburg  
E-mail: theato@chemie.uni-hamburg.de

Prof. H. Yoon<sup>[†]</sup>  
Department of Chemical Engineering, Seoul National  
University of Science & Technology, Seoul, 139-743, Korea

Dr. N. Haberkorn  
Institute of Organic Chemistry, University of Mainz,  
Duesbergweg 10-14, 55099 Mainz, Germany  
H.-J. Song, Prof. C. H. Lee  
School of Electrical Engineering and Computer Science,  
Inter-University Semiconductor Research Center (ISRC), Seoul  
National University, Seoul, 151-744, Korea  
[†] T. Kim and H. Yoon contributed equally to this work.

highly efficient organic photovoltaic cells, due to the ordered interpenetrating network of donor or acceptor nanorods surrounded by continuous acceptor or donor phase at the nanometer-scale.<sup>[4]</sup> Predominantly, poly(3-hexylthiophene) (P3HT) and ([6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM)) bulk heterojunctions have been investigated as materials of choice for OPV cells.<sup>[1–3]</sup> However, it still remains a daunting task to control the order of P3HT in the PCBM phase in bulk heterojunction OPV cells and thus to control the internal interfacial area. For this reason, several approaches have been reported to produce OBHJ OPVs, most notably with nanoimprint lithography (NIL).<sup>[5–16]</sup> NIL has been employed by several groups utilizing AAO templates<sup>[5–10]</sup> or Si molds.<sup>[11–15]</sup> The technique has the advantage of realizing large-area nanostructures without resolution limit. Furthermore, it has been reported that chains of conducting polymers tend to align themselves within such confined geometry during the nanoimprint process, resulting in an enhanced hole mobility when compared with randomly oriented P3HT in BHJ solar cells.<sup>[5]</sup>

All in all, the NIL process is regarded as the most suitable method to prepare ordered bulk heterojunction OPVs. However, contaminations with remaining ions and possible damage of solar cell components (either P3HT or PCBM) during the template removal are serious problems for solar cell performance and, thus, the development of a new and reliable continuous manufacturing nanoimprint lithographic process is absolutely vital. Furthermore, a roll-to-roll process is suitable and appears to be inevitable for the continuous large-area fabrication at low cost.<sup>[17]</sup> But in the case of the roll-to-roll process, a flexible mold or substrate must be used.<sup>[18]</sup> The most well-known flexible replica molds are made of poly(dimethyl siloxane) (PDMS).<sup>[19]</sup> However, those PDMS molds have moduli too low ( $\approx 2$  MPa) to transfer nanopatterns of polymers such as P3HT.<sup>[20]</sup> Furthermore, a low surface energy of molds is required to release nanopatterns such as nanopillars easily from the molds, enabling the roll-to-roll process. Moreover, PDMS molds are easily swollen with organic solvents when P3HT solution is applied to PDMS molds. All these points should be urgently addressed to solve the mass production of OBHJ OPVs.

In this work, we present a strategy for a low-cost fabrication process of ordered OPVs by employing a direct transfer method of P3HT with a rigiflex<sup>[21–23]</sup> and reusable replica mold obtained from a self-assembled AAO template. The polymeric rigiflex molds could assure the transfer of nanostructures below 100 nm by increasing moduli of the molds but yet providing enough flexibility for conformal contacts on substrates with inherent roughness. Using polyfluoropolyether (PFPE)<sup>[24,25]</sup> as a replica mold material, which provides the low surface energy as well as the strong resistance to swelling in organic

solvents, the transfer characteristics of P3HT nanostructures onto PEDOT/PSS-coated ITO substrates will be studied. To reduce the fabrication cost of masters in large area, we employed well-ordered anodic aluminum oxide (AAO) as a template. Consequently, this patterning process demonstrates the possibility to reproducibly prepare well-defined ordered bulk heterojunction OPVs using reusable PFPE molds. We believe that the processing method based on regiflex molds proposed here has the advantage of lower pressure and processing temperature when compared with the traditional nanoimprint lithography, laying the foundation for the roll-to-roll process required for the mass production of ordered bulk heterojunction OPVs. In addition, the realization of complementary nanopillars or nanocavities of P3HT by the self-replication of replica molds will also be discussed.

## 2. Experimental Section

### 2.1. Preparation of Anodized Aluminum Oxide Template

Hexagonally ordered porous AAO templates were fabricated via two-step anodization of aluminum foils (99.999%; Goodfellow). Aluminum foils were degreased with acetone to remove organic impurities and mounted on a copper plate serving as the anode. Aluminum foils were partially exposed to an acid in a thermally isolated cell. Aluminum foils were electropolished in a 1:3 volume mixture of  $\text{HClO}_4$  and  $\text{C}_2\text{H}_5\text{OH}$ . Then, the foils were anodized under constant voltage (40 V) by power supply (Agilent Technologies N5700) with 0.3 M oxalic acid electrolyte for more than 4 h while the temperature was fixed at 15 °C. After the first anodization, the aluminum oxide layer was removed by a chemical etching in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 45 °C for more than 6 h. Subsequently, the second anodization was performed under the same conditions to the first anodization.

### 2.2. Surface Modification of AAO Template

To release the polymeric replica molds from AAO templates, a surface modification of AAO template was prerequisite. The surface of the AAO templates was treated following a previously reported procedure.<sup>[26]</sup> Briefly, the surface of an AAO template was first treated with oxygen plasma (25 W, 3 min, 1 sccm of  $\text{O}_2$ ) (Mini plasma-Cube). Then, AAO was immersed in a 0.5 wt% aqueous solution of 3-(aminopropyl triethoxysilane) (APTES; Aldrich) for 10 min. After washing with distilled water, the surface AAO was reacted with monoglycidyl ether-terminated polydimethylsiloxane (PDMS; Aldrich) at 80 °C. After reacting for 4 h, the modified AAO was cleaned by ultrasonic treatment in isopropyl alcohol for 1 min to remove any unreacted PDMS.

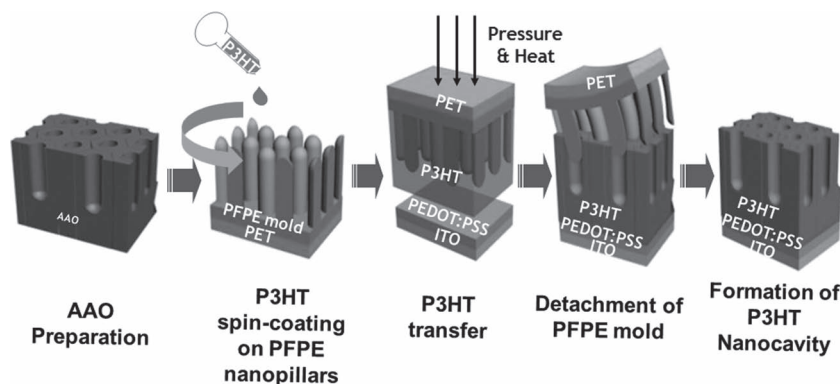
### 2.3. Preparation of Rigiflex Replica Molds

Nanopillar-patterned PFPE replica molds were prepared from AAO templates by dispensing a mixture of PFPE prepolymers

(5101X, Fluorolink) and initiator onto the prepared AAO template. After UV exposure through transparent poly(ethylene terephthalate) (PET) film used as a backplane, the PFPE replica mold was detached from the surface-modified AAO template. Further UV exposure was performed for several hours to eliminate unreacted precursors. To prepare negative-type of PFPE molds (nanocavity), at first, we prepared PUA (311RM, Minuta Tech.) nanopillar-patterned first replica mold from the AAO template. And then, PFPE (MD700, Fluorolink) prepolymer mixture was dispensed onto the first PUA replica mold. After UV curing, the PFPE nanocavity-shaped PFPE replica mold (second replica mold) could be detached from the PUA nanopillar-shaped first replica mold. All nanostructures were characterized by a field emission-scanning electron microscope (FESEM, JSM-74F).

#### 2.4. Device Fabrication and Characterization

First, we cleaned ITO-coated glass substrates through ultrasonication in acetone, isopropanol, and distilled water for 20 min, respectively. The substrates were then treated by UV ozone (AH-1700, AHTECH) to make the surface hydrophilic. Onto these substrate, PEDOT:PSS (H. C. Starck) was spincoated with 4000 rpm and baked for 30 min at 130 °C. P3HT nanostructures (nanopillars or nanocavities) were obtained by spincoating P3HT (4002-EE, Rieke Metals) solution (0.5 ≈ 1 wt%) in chloroform on the prepared PFPE replica molds, followed by transferring the P3HT films (100 ≈ 110 nm thickness) on the PFPE mold to the PEDOT:PSS-coated substrates with heat (120 °C) and pressure (4 bar). After cooling down to room temperature, the PFPE replica mold were detached from patterned P3HT layers adhering on the substrate. PC<sub>60</sub>BM (Nano-C) was spin coated in orthogonal solvent (dichloromethane, 1 wt%) on the P3HT nanostructure. It is noted that we used a P3HT with high molecular weight ( $M_n = 50$  K) to prevent the total dissolution by dichloromethane.<sup>[16]</sup> Although there was a slight deformation of P3HT nanostructures because of partial dissolution of low-molecular-weight P3HT (polydispersity = 2.0 ≈ 2.4) after spincoating of dichloromethane, the P3HT maintained their structures as shown in Figure S1 (Supporting Information). The thickness of PCBM was about 80 nm. To improve contact between P3HT nanostructures and PCBM overlayers, the samples were pressed with a flat PDMS block at 80 °C for 10 min. Then, 5 Å of LiF and 100 nm of aluminum films were thermally evaporated to form the top contacts. After fabrication of the devices, they were thermally annealed (80 °C) in N<sub>2</sub> atmosphere for 10 min. The active area of solar cell was 0.2 cm<sup>2</sup>, given by the overlap area between ITO and Al electrodes. Current density–voltage (J–V) characteristics of the devices were measured with a source measurement unit (Keithley SMU237). The device performances were characterized under AM 1.5G condition with an illumination intensity of 100 mW cm<sup>-2</sup> using a solar simulator (Newport 91160A).



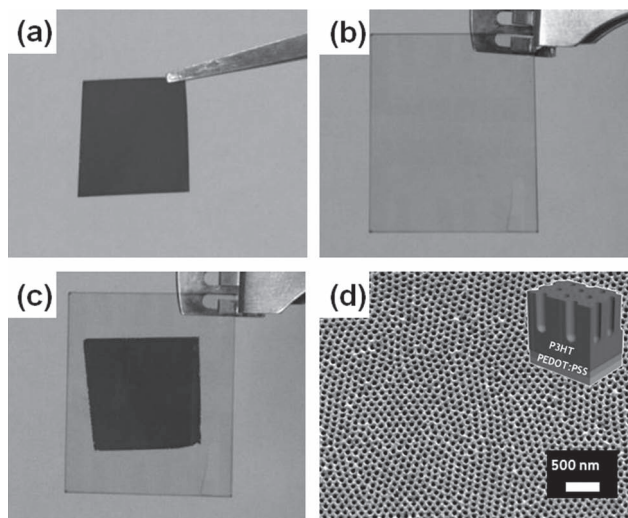
**Figure 1.** A schematic illustration to realize a P3HT nanocavity structure by the transfer molding method from a rigid PFPE mold.

### 3. Results and Discussion

Figure 1 schematically represents the fabrication of P3HT nanocavities by the transfer method from a rigid PFPE replica mold.<sup>[22]</sup> First, a PFPE replica mold was prepared from a PDMS-grafted AAO template.<sup>[24]</sup> The PFPE replica mold then has a nanopillar structure, exactly molded from the nanocavity structure of the AAO template. Noteworthy, PFPE has a sufficiently high modulus ( $\approx 160$  MPa) to retain the high aspect-ratio nanopillars obtained from the AAO template.<sup>[24]</sup> Next, voids of the PFPE replica mold were filled with P3HT by dispensing a P3HT solution onto the prepared PFPE rigid replica mold for 1 min to completely fill the voids by the capillary force. The P3HT solution was additionally spin-coated to guarantee a flat, uniform, and controllable thickness of the P3HT film. Due to the strong resistance of PFPE against many common organic solvents, the PFPE replica mold was neither swollen nor distorted during the filling and spin-coating processes,<sup>[24,25]</sup> which would be the major problems when using PDMS replica molds. Finally, the P3HT nanocavity film — still kept inside the nanopillar-shaped PFPE replica mold (Figure 2a) — was transferred onto a PEDOT/PSS-coated ITO substrate (Figure 2b). Because of the low surface energy of PFPE (17.7 mN m<sup>-1</sup>), the adhesion between the PFPE mold and P3HT is weaker than the adhesion between P3HT and PEDOT/PSS. Consequently, the PFPE replica mold could easily be detached and recycled, leaving behind the P3HT nanocavity structure adhered to the ITO substrate (Figure 2d). Figure 2d shows a tilted scanning electron microscope (SEM) image of the P3HT nanocavity structures.

It has to be noted that chloroform was used as a solvent for the P3HT solution. An attempt to use chlorobenzene, which is regarded as a typical solvent for P3HT, resulted in unstable or partially dewetted films presumably due to the low surface energy of the PFPE mold as shown in Figure S2 (Supporting Information). Figure 2c shows the defect-free transfer of the nanostructured P3HT film onto an ITO substrate. As a result, the PFPE mold as the original master is

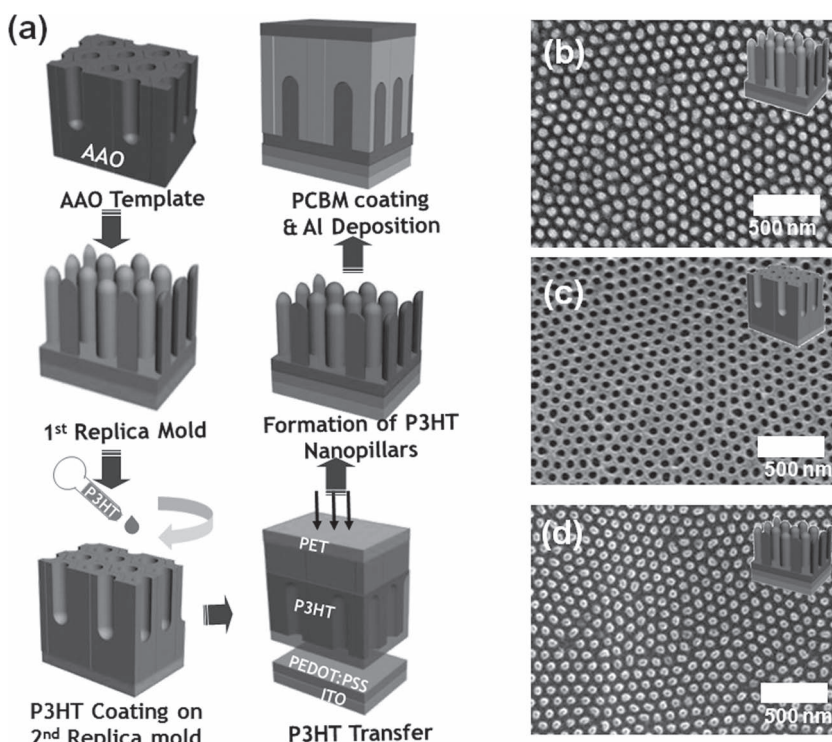




**Figure 2.** (a) A picture of the PFPE mold filled and spin-cast with P3HT. (b) A picture of PEDOT:PSS-coated substrate before transferring a P3HT film. The substrate has a size of 24 mm × 20 mm. (c) A picture of the ITO substrate after the transfer of the P3HT nanostructured film. (d) A tilted SEM image of the P3HT nanocavity-structured film.

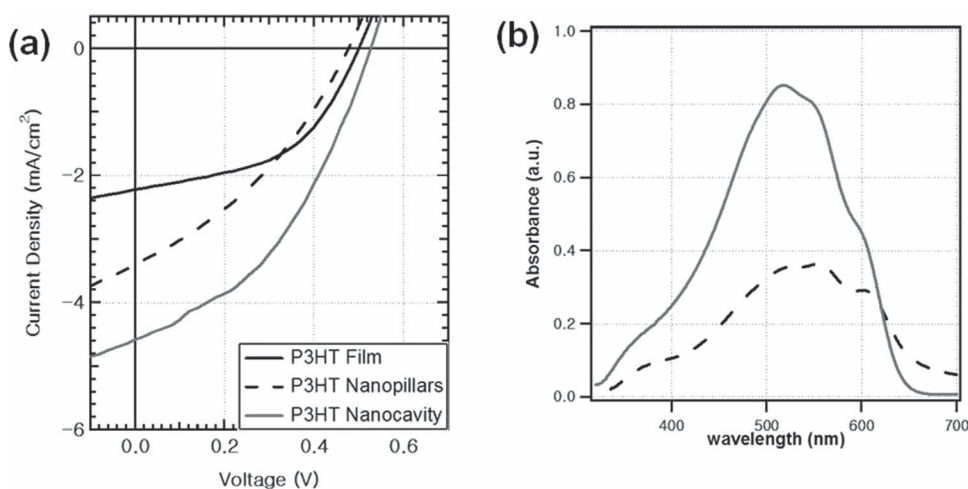
preserved and could be repeatedly used to make multiple replicas of nanostructured P3HT films, which is critically important to reduce materials and processing cost.

The use of PFPE molds has additional advantages over employing stiff silicon or AAO templates as molds. Silicon or AAO molds typically require high pressure to guarantee the conformal contact between the mold and a P3HT-covered glass (ITO) substrate. Particularly, inherent roughness on the micro-scale of AAO templates not only requires high pressure to contact the entire surface of the AAO against the rigid substrate but also results in the breakage of nanopillar patterns during the transfer. The rigiflex replica mold, used in the present study, is sufficiently flexible to enable the conformal contact at relative low pressure (less than 4 bar), but provides enough rigidity to produce high aspect-ratio nanopillar patterns from the AAO templates. The flexibility of the replica mold represents the fundamental basis for the roll-to-roll process enabling fast-prototype large-area fabrication. The low process temperature below 120 °C for the fabrication of organic devices is also a benefit especially when we use a flexible polymeric material as a substrate.



**Figure 3.** (a) A schematic illustration for the fabrication of ordered bulk heterojunction solar cells with P3HT nanopillars by the two-step replication. (b) A SEM image of the first PUA nanopillar replica mold. (c) A SEM image of the second PFPE nanocavity replica mold. (d) A SEM image of P3HT nanopillars transferred from the second PFPE replica mold.

Another advantage of using rigiflex replica molds is the self-replication of molds with sub-100 nm features. A negative-type PFPE replica mold featuring nanocavities was realized by a two-step replication from the original AAO template (Figure 3), allowing the fabrication of P3HT nanopillar structures. Figure 3a schematically shows the procedure to realize P3HT nanopillars from the second PFPE replica mold based on the two-step replication, resulting in OBHJ solar cells with the P3HT nanopillars obtained. A poly(urethane acrylate) (PUA (311RM), Minuta Ltd.)<sup>[22]</sup> nanopillar replica mold was prepared by the UV crosslinking of the liquid prepolymer dispensed into an AAO template (Figure 3b). After detaching the cured PUA replica mold from the AAO template, we exposed the replica mold to UV for the complete crosslinking of the replica mold. Then, PFPE precursors (MD700, Fluorolink) were deposited onto the first PUA replica mold. The UV crosslinking and detachment of PFPE from the first replica mold resulted in the second PFPE replica mold with nanocavities (Figure 3c). Likewise, the second PFPE replica mold has served as the template to prepare P3HT nanopillars, which were then transferred onto a PEDOT/PSS-coated ITO substrate (Figure 3d). In all cases, the inter-pore distance as well as the diameter of nanocavities and nanopillars was kept almost constant at  $\approx 105$  and  $\approx 54$  nm, respectively.



**Figure 4.** (a) Current density–voltage ( $J$ – $V$ ) characteristics of OPV cells prepared from P3HT nanopillars (dashed line), nanocavities (gray solid line) and flat bilayer films (black solid line). (b) UV–Vis absorbance spectra of P3HT nanopillars (dashed line) and nanocavities (gray solid line).

After successful preparation of two complementary P3HT nanostructures (i.e., nanopillars and nanocavities), ordered bulk heterojunction solar cells were finally prepared by spin coating a PCBM solution (1 wt% in dichloromethane) on the top of respective P3HT nanostructures. To improve the interfacial contact between P3HT nanostructures and PCBM, the PCBM layers were pressed with a flat PDMS block (ca. 4 bar, 80 °C for 10 min). Then, 5 Å of LiF and 100 nm of aluminum films were thermally evaporated to form the top electrode contacts. As a reference OPV cell, a P3HT film was spin-coated on a flat and unstructured PFPE mold, transferred onto a PEDOT/PSS-coated substrate, and then spincoated with PCBM to realize a bilayer system. All the OPV cells were subsequently annealed at 80 °C to improve the contacts between P3HT and PCBM phases prior to the cell characterization. Figure 4a shows the current density–voltage ( $J$ – $V$ ) characteristics of the OPV cells prepared from P3HT nanopillars, nanocavities, and flat bilayer films. For both nanostructured OBHJ OPV cells, higher current densities and efficiencies were obtained when compared with the flat bilayer film. We also note that the ordered bulk heterojunction solar cell with P3HT nanocavities has the higher current density and efficiency ( $J_{sc} = 4.58 \text{ mA cm}^{-2}$ , PCE = 0.98%) than the devices based on P3HT nanopillars ( $J_{sc} = 3.41 \text{ mA cm}^{-2}$ , PCE = 0.56%) and the flat bilayer film ( $J_{sc} = 2.21 \text{ mA cm}^{-2}$ , PCE = 0.55%). To explain the difference in the current density between P3HT nanopillars and nanocavities, we measured the UV–Vis absorbance of both nanostructured films. As shown in Figure 4b, the total absorbance of the P3HT nanocavity-based film is at least two times higher than the absorbance with the nanopillar-based device although the location of peaks are almost same between two different structures. To

explain the difference of the absorbance, we compared the volume fraction of P3HT in two structures. In the present work, we used an AAO template prepared by the anodization in oxalic acid with the interpore distance ( $D_{int}$ ) of 105 nm, the pore diameter  $D_p$  of 54 nm, and the pore depth of 125 nm. The porosity of a hexagonal structure with cylindrical pores is simply given by:

$$porosity = \frac{\pi}{2\sqrt{3}} \left( \frac{D_p}{D_{int}} \right)^2 \quad (1)$$

Therefore, the porosity of the nanocavity-patterned P3HT film is estimated to be 24% while the porosity of the nanopillar-based P3HT film is about 76%. Although both structures have identical interfacial areas between P3HT and PCBM, the photovoltaic cell fabricated from the nanocavity-patterned P3HT film should yield higher UV–Vis absorption due to the higher volume fraction of P3HT with the nanocavity film, resulting in the increased amount of charge carriers. This difference in the volume fraction of P3HT is ultimately reflected on the results of both  $J$ – $V$  curves (Figure 4a) and absorption spectra (Figure 4b).

#### 4. Conclusion

We presented a strategy for a low-cost fabrication process of ordered OPVs by employing a direct transfer method of P3HT with a rigiflex and reusable replica mold obtained from a self-assembled AAO template. The low surface energy as well as the strong resistance to common organic solvents of the PFPE replica molds allowed easy and successful transfer of nanostructured P3HT films onto PEDOT/PSS-coated ITO substrates. Furthermore, we obtained P3HT nanopillar structure as well as P3HT nanocavity structure by exploiting the self-replication of replica molds. Even

though the different P3HT nanostructures virtually have the identical interfacial contact area, different device performance was observed, thereby motivating further fundamental investigation on such ordered bulk heterojunction OPVs. Consequently, this new patterning process demonstrates, the possibility to reproducibly prepare well-defined ordered bulk heterojunction OPVs using reusable PFPE molds and also to effectively eliminate potential ionic impurities commonly caused by the direct dissolution of AAO or Si templates, which would deteriorate the device performance. Thus, a firm foundation is herewith laid down for a continuous fabrication process of ordered bulk heterojunction OPVs.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements:** This work was financially supported by the National Research Foundation of Korea (NRF) Grants through the National Creative Research Initiative Center for Intelligent Hybrids (2010-0018290) and the WCU Program of Chemical Convergence for Energy & Environment (R31-10013), the Brain Korea 21 Program funded by the Ministry of Education, Science and Technology (MEST), and the German Science Foundation DFG (IRTG 1404).

Received: July 24, 2012; Revised: August 10, 2012; Published online: September 19, 2012; DOI: 10.1002/marc.201200503

**Keywords:** large-area fabrication; nanocavities; nanopillars; organic solar cells; P3HT

- [1] S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324.
- [2] G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, *21*, 1323.
- [3] K. M. Coakley, M. D. McGehee, *Chem. Mater.* **2004**, *16*, 4533.
- [4] N. Haberkorn, M. C. Lechmann, B. H. Sohn, K. Char, J. S. Gutmann, P. Theato, *Macromol. Rapid Commun.* **2009**, *30*, 1146.
- [5] J. S. Kim, Y. Park, D. Y. Lee, J. H. Park, J. K. Kim, K. Cho, *Adv. Funct. Mater.* **2010**, *20*, 540.
- [6] N. Haberkorn, S. Kim, K.-S. Kim, M. Sommer, M. Thelakkat, B.-H. Sohn, P. Theato, *Macromol. Chem. Phys.* **2011**, *212*, 2142.
- [7] N. Haberkorn, S. A. L. Weber, R. Berger, P. Theato, *ACS Appl. Mater. Interfaces* **2010**, *2*, 1573.
- [8] S. A. L. Weber, N. Haberkorn, P. Theato, R. Berger, *Nano Lett.* **2010**, *10*, 1194.
- [9] N. Haberkorn, J. S. Gutmann, P. Theato, *ACS Nano* **2009**, *3*, 1415.
- [10] D. Chen, W. Zhao, T. P. Russell, *ACS Nano* **2012**, *6*, 1479.
- [11] X. He, F. Gao, G. Tu, D. Hasko, S. Hüttner, U. Steiner, N. C. Greenham, R. H. Friend, W. T. S. Huck, *Nano Lett.* **2010**, *10*, 1302.
- [12] X. He, F. Gao, G. Tu, D. Hasko, S. Hüttner, N. C. Greenham, U. Steiner, R. H. Friend, W. T. S. Huck, *Adv. Funct. Mater.* **2011**, *21*, 139.
- [13] M. Aryal, K. Trivedi, W. Hu, *ACS Nano* **2009**, *3*, 3085.
- [14] M. S. Kim, J. S. Kim, J. C. Cho, M. Shtein, L. J. Guo, J. Kim, *Appl. Phys. Lett.* **2007**, *90*, 123113.
- [15] M. Aryal, F. Buyukserin, K. Mielczarek, X. M. Zhao, J. Gao, A. Zakhidov, W. Hu, *J. Vac. Sci. Technol. B* **2008**, *26*, 2562.
- [16] Y. Yang, K. Mielczarek, M. Aryal, A. Zakhidov, W. Hu, *ACS Nano* **2012**, *6*, 2877.
- [17] J. W. Jung, W. H. Jo, *Adv. Funct. Mater.* **2010**, *20*, 2355.
- [18] H. Yoon, T. I. Kim, S. J. Choi, K. Y. Suh, M. J. Kim, H. H. Lee, *Appl. Phys. Lett.* **2006**, *88*, 254104.
- [19] Y. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* **1998**, *37*, 550.
- [20] C. Y. Hui, A. Jagota, Y. Y. Lin, E. J. Kramer, *Langmuir* **2002**, *18*, 1394.
- [21] D. Suh, S. J. Choi, H. H. Lee, *Adv. Mater.* **2005**, *17*, 1554.
- [22] S. J. Choi, P. J. Yoo, S. J. Baek, T. W. Kim, H. H. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 7744.
- [23] J. P. Rolland, R. M. V. Dam, D. A. Schorzman, S. R. Quake, J. M. Desimone, *J. Am. Chem. Soc.* **2004**, *126*, 2322.
- [24] S. H. Sung, H. Yoon, J. Lim, K. Char, *Small* **2012**, *8*, 826.
- [25] S. S. Williams, M. J. Hampton, V. Gowrishankar, I. K. Ding, J. L. Templeton, E. T. Samulski, J. M. DeSimone, M. D. McGehee, *Chem. Mater.* **2008**, *20*, 5229.
- [26] M. K. Choi, H. Yoon, K. Lee, K. Shin, *Langmuir* **2011**, *27*, 2132.