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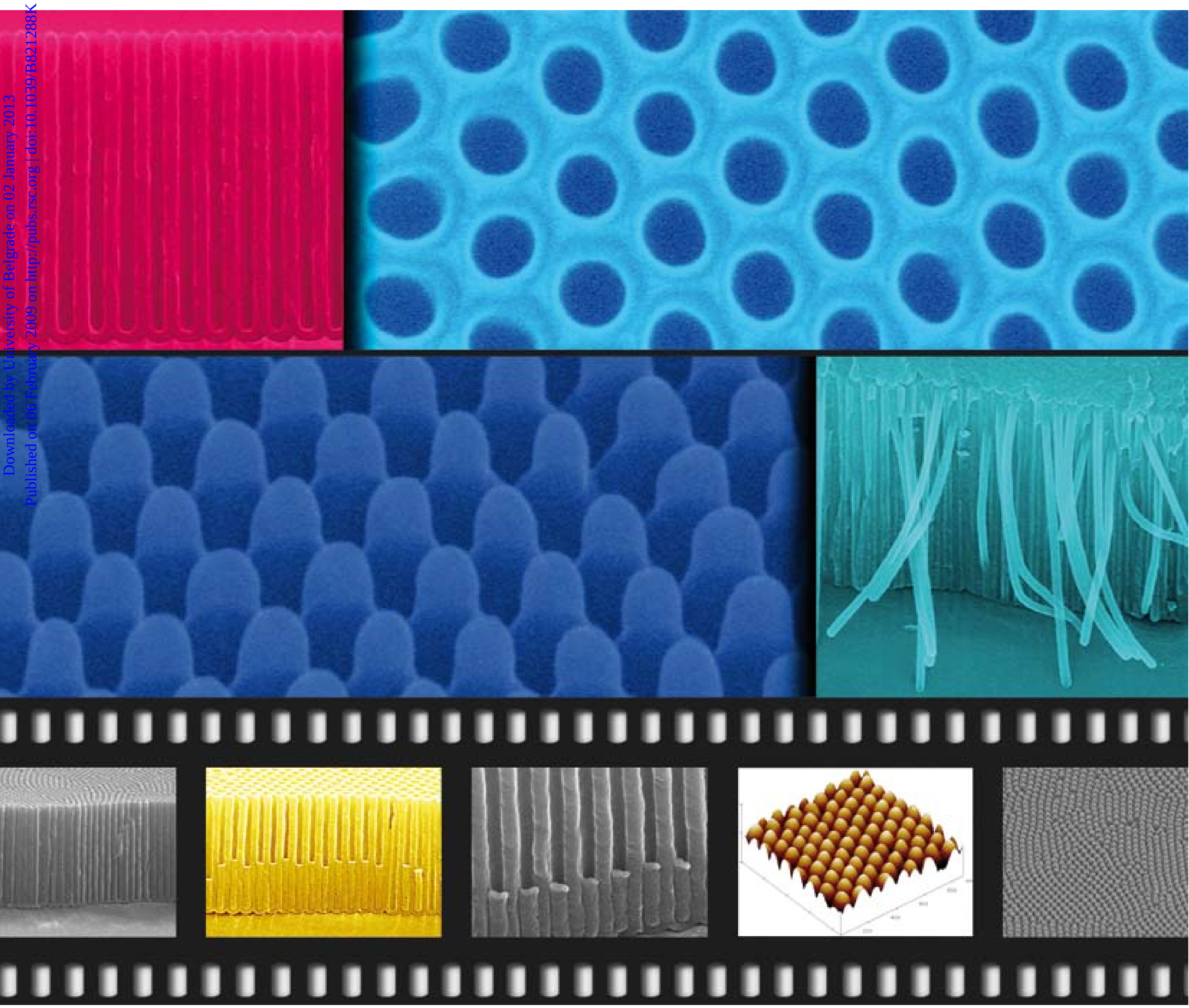

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PAPER
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A facile method to prepare regioregular poly(3-hexylthiophene) nanorod arrays using anodic aluminium oxide templates and capillary force

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Regioregular poly(3-hexylthiophene) (RR-P3HT) nanorod arrays were prepared on the indium tin oxide (ITO) substrate by capillary force in a vacuum oven (0.855 torr, 250 °C) using a drop-coating of RR-P3HT and anodic aluminium oxide (AAO) templates. The AAO templates were prepared by a two step anodizing process in an oxalic acid electrolyte. The templates had a highly ordered structure with a uniform pore diameter of ∼55–80 nm and cell lengths of ∼100–3930 nm. With suitable temperature and capillary force in the vacuum oven, the drop-coated RR-P3HT solution infiltrated the AAO templates. After removal of the AAO template, the RR-P3HT has a nanorod array form, with diameters of ∼55 nm and heights of ∼70 nm.

Introduction

The design and modification of conjugated polymers have attracted considerable interest in both fundamental studies and applied research.[1–5] Conjugated polymers have many advantages over low molecular weight organic and inorganic materials.[6–10] In addition, conjugated polymers offer the advantages of low cost and flexibility of use. Furthermore, the physical, chemical, and electrical properties of polymers can be easily controlled by changing the molecular structure and weight of the polymer. Conjugated polymers have been used in electrical devices, optical systems, and various sensor applications.[11–15]

The surface morphology of a polymer on an electrode should be considered to develop efficient nanoscale devices based on the polymer. Not surprisingly, the performance of polymer devices is strongly influenced by the surface morphology of the polymer on the electrode.[16–20] Among numerous strategies in the design and modification of polymer surface morphology, one-dimensional structures including nanowires, nanotubes, and nanorods have attracted great attention in the field of nanoscale devices.[21–24]

One-dimensional structural materials can help enhance electron transport by avoiding the particle-to-particle hopping that occurs in titanium oxide networks and hybrid polymer solar cells.[25,26] Moreover, the morphology of the one-dimensional structure can improve the possibility that all electrons have a direct connection to the collection electrode.[27–29] Joo and colleagues reported the synthesis of nanotubes and nanowires of poly(3-methylthiophene) (P3MT) using a nanoporous anodic aluminium oxide (AAO) template through an electrochemical polymerization method.[28,29] Using scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques, they observed the formation of nanotubes with diameters of 100–200 nm and wall thicknesses of 5–10 nm. Relatively long nanotubes and nanowires of P3MT (∼40 μm in length) were obtained.[28] However, although a number of interesting strategies have been developed and examined in this context over the past several decades, the design and modification of the surface morphology of the polymer has not yet been fully understood. To date, formation of regioregular poly(3-hexylthiophene) (RR-P3HT) nanorod arrays on the indium tin oxide (ITO) substrate using an AAO template and capillary force has not been reported. Compared to other conjugated polymers, RR-P3HT has many unique properties. The charge carrier mobility of RR-P3HT at room temperature is higher than that of regiorandom P3HT.[30,31] In addition, RR-P3HT is of particular interest due to its self-organizing properties to form a microcrystalline structure.[30,31] To date, RR-P3HT appears to be one of the most suitable conjugated polymers for nanoscale devices.

With the aid of our previous research concerning the design and modification of polymers,[32–35] in this paper, we describe a facile methodology for the formation of RR-P3HT nanorod arrays on the ITO substrate using an AAO template and capillary force in a vacuum oven.

Results and discussion

Formation of RR-P3HT nanorods in AAO templates with various pore diameters

The formation of RR-P3HT nanorod arrays in AAO templates resulted from capillary forces in a vacuum oven. Fig. 1 shows SEM images of AAO templates with cell lengths of ∼1000 nm and various pore diameters. To control the pore diameters of the AAO templates, the pore widening time was varied between 60, 75, 90, 105, and 120 min. As shown in Fig. 1,

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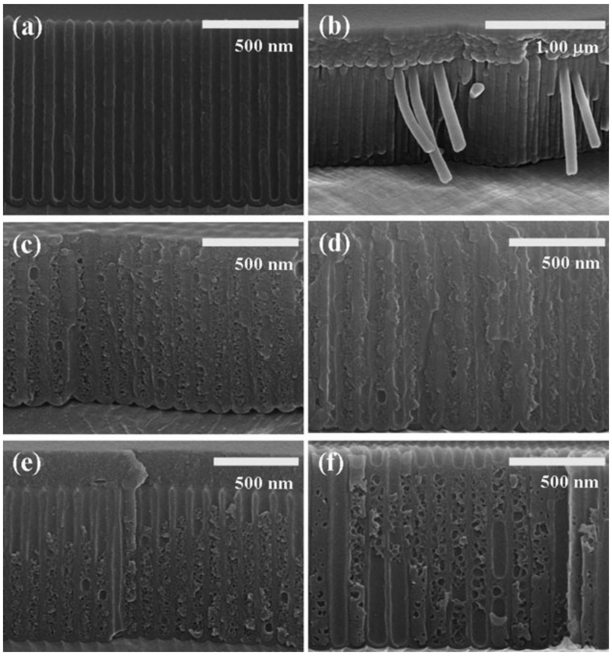


Fig. 1 SEM images of (a) an AAO template and (b–f) RR-P3HT nanorods in AAO templates with various pore diameters (cell length of 1000 nm): (a, b) 55, (c) 60, (d) 70, (e) 75, and (f) 80 nm.

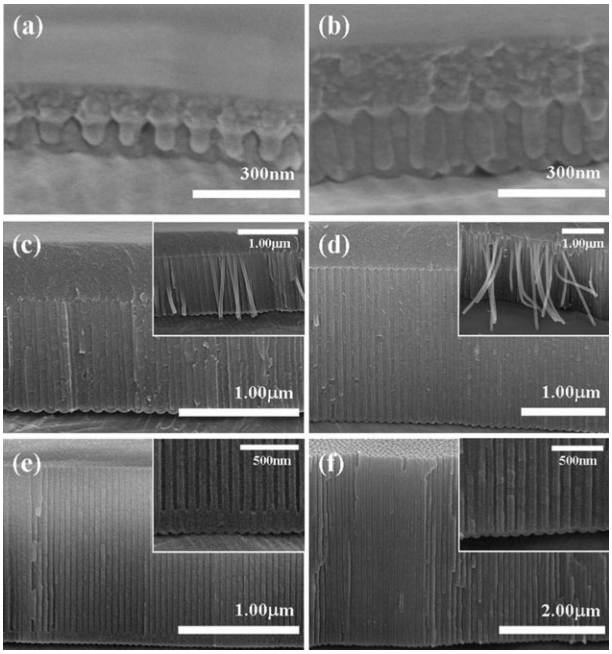


Fig. 2 SEM images of RR-P3HT nanorods in AAO templates with various cell lengths (pore diameter of 55 nm): (a) 100, (b) 220, (c) 1000, (d) 1850, (e) 2950, and (f) 3930 nm.

the pore diameters of the AAO templates were approximately (a, b) 55 (60 min), (c) 60 (75 min), (d) 70 (90 min), (e) 75 (105 min), and (f) 80 nm (120 min). Fig. 1(a) shows an AAO template itself and Fig. 1(b–f) displays AAO templates filled with RR-P3HT.

The RR-P3HT nanorods were successfully formed by capillary force in a vacuum oven (0.855 torr, 250 °C). The capillary force phenomenon can be equated as the height of a liquid column (h), as expressed by the following capillary action formula.[36]

$$h = 2\gamma \cos\theta/\rho g r \qquad (1)$$

Here, γ is the liquid–air surface tension (J m^{-2} or N m^{-1}), θ is the contact angle, ρ is the density of liquid (kg m^{-3}), g is acceleration due to gravity (m s^{-2}), and r is the radius of the tube (m). According to this formula, the length of the RR-P3HT nanorods in the AAO templates (h) is inversely proportional to the pore diameter ($2r$) of the AAO template. Therefore, the pore sizes of the AAO templates influence the infiltration of RR-P3HT solutions into the AAO templates.

Formation of RR-P3HT nanorods in AAO templates with various cell lengths

Fig. 2 shows SEM images of RR-P3HT nanorods in AAO templates with various cell lengths. The cell lengths of the AAO templates were controlled by varying the 2nd anodization time. As shown in Fig. 2, the cell lengths of the AAO templates were approximately (a) 100 (2 min), (b) 220 (5 min), (c) 1000 (30 min), (d) 1850 (60 min), (e) 2950 (90 min), and (f) 3930 nm (120 min). Up to a cell length of 1850 nm, the RR-P3HT solutions filled the AAO templates by capillary force in a vacuum oven. However, the RR-P3HT solution could not fill the AAO templates by capillary force when the cell length was in excess of 1850 nm. This is attributed to a limitation of the capillary force when the cell length is long.

Effect of RR-P3HT concentration and solvents

Not surprisingly, the formation of RR-P3HT nanorods was strongly influenced by the concentration of RR-P3HT in

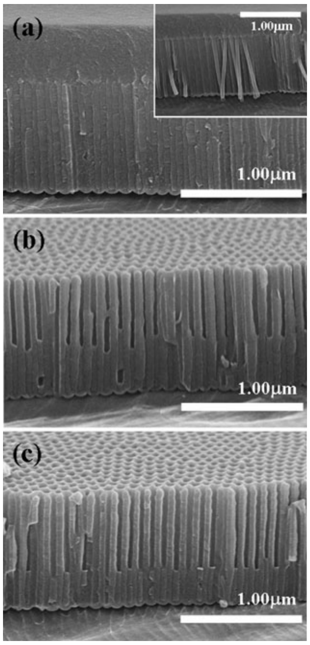


Fig. 3 SEM images of RR-P3HT nanorods in AAO templates formed with (a) 2, (b) 4, and (c) 6 w/v% RR-P3HT solutions in chlorobenzene.

solution. Fig. 3 shows SEM images of RR-P3HT nanorods in AAO templates with various concentrations of RR-P3HT when chlorobenzene was used as a solvent. At the low concentration of 2 w/v% shown in Fig. 3(a), the RR-P3HT solution completely penetrated the pores of the AAO template. However, at the higher concentrations of 4 and 6 w/v% shown in Fig. 3(b) and (c), respectively, the AAO templates were not fully filled and RR-P3HT nanorods were formed at ~400 nm (4 w/v%) and ~280 nm (6 w/v%). According to the capillary action formula (eqn (1)), the length of the RR-P3HT nanorods in the AAO template (*h*) is inversely proportional to the density of the liquid (ρ). Therefore, it can be understood that unsuccessful filling of RR-P3HT in the AAO template is due to their density, which is directly proportional to the concentration of the RR-P3HT solution.

The formation of RR-P3HT nanorods was also strongly influenced by the solvent used. In order to confirm the effects of the solvent, RR-P3HT was dissolved in chlorobenzene, toluene, and 1,2-dichlorobenzene. Fig. 4(a–c) shows SEM images of RR-P3HT nanorods formed using chlorobenzene, toluene, and 1,2-dichlorobenzene, respectively. As discussed with regards to the effect of concentration, with chlorobenzene solvent RR-P3HT nanorods were completely formed into the pores of the AAO template. However, when compared to chlorobenzene, poorly-shaped RR-P3HT nanorods were obtained in AAO templates when toluene and 1,2-dichlorobenzene were used as solvents. The filling of the RR-P3HT solution into the AAO template seems to be affected by the wetting energy between the RR-P3HT solution and the ITO substrate that the AAO templates are placed on.

In the case of chlorobenzene solvent, the wetting energy is 64.61 mN m^{-1}. However, the wetting energies of toluene and 1,2-dichlorobenzene are 68.25 mN m^{-1} and 68.20 mN m^{-1}, respectively. Compared to toluene and 1,2-dichlorobenzene, the wetting energy between the RR-P3HT solution and the ITO substrate in chlorobenzene is decreased, which facilitates easy filling of the RR-P3HT solutions into the AAO templates. Accordingly, the pores of the AAO template were well-filled using the RR-P3HT solution in chlorobenzene as compared to toluene and 1,2-dichlorobenzene.

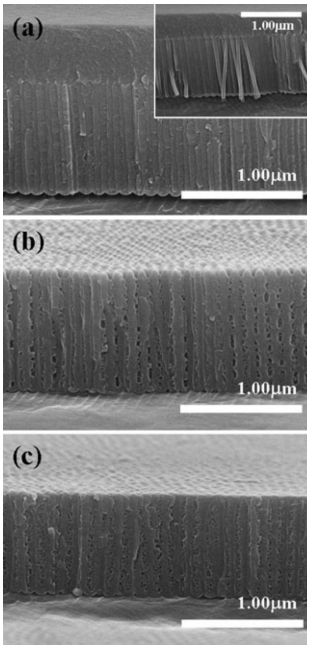


Fig. 4 SEM images of RR-P3HT nanorods in AAO templates formed using 2 w/v% RR-P3HT in (a) chlorobenzene, (b) toluene, and (c) 1,2-dichlorobenzene solutions.

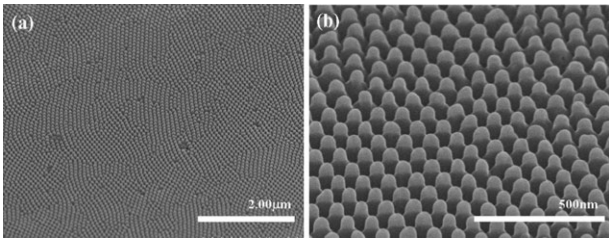


Fig. 5 SEM images of RR-P3HT nanorod arrays on the ITO substrate without an AAO template.

Surface morphology and optical properties of RR-P3HT nanorod arrays on the ITO substrate after removing the AAO templates

In order to obtain RR-P3HT nanorod arrays, AAO templates were removed using a NaOH solution.[28] The surface morphology of the RR-P3HT nanorod arrays on the ITO substrate without the AAO template is shown in Fig. 5. These were prepared using an AAO template with a cell length of ~100 nm and a pore diameter of ~55 nm. Large area, non-collapsed, and vertically aligned RR-P3HT nanorod arrays with average heights of ~70 nm and widths of ~55 nm were successfully obtained on the ITO substrate. Fig. 6 shows absorption spectra of the nanorod arrays and a spin coated film of RR-P3HT. The absorption coefficient over a wavelength of 520 nm, particularly on the red shoulder at 600 nm, increases for nanorod arrays.[37] This indicates that the degree of the RR-P3HT chain packing increases in nanorod arrays resulting in a higher crystallinity than the spin coated film.

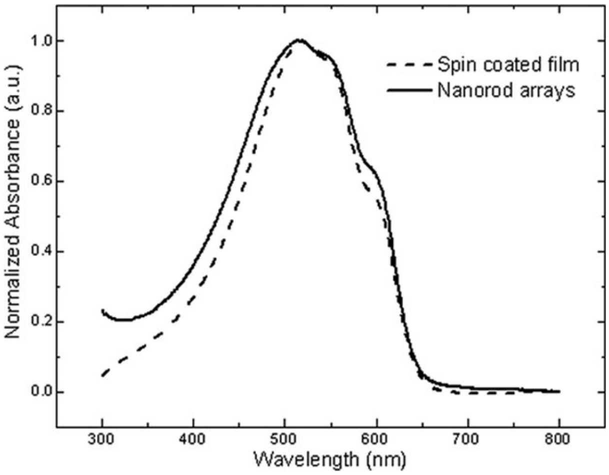


Fig. 6 Absorption spectra of nanorod arrays and a spin coated film of RR-P3HT.

Conclusions

In conclusion, AAO templates were prepared under different pore diameters and cell lengths. The AAO templates, prepared by a two step anodizing process in oxalic acid electrolyte, had a highly ordered structure with a uniform pore diameter of ~55–80 nm and cell lengths of ~100–3930 nm. These AAO templates were placed on drop-coated RR-P3HT films on the ITO substrate in a vacuum oven (0.855 torr, 250 °C) in order to prepare PP-P3HT nanorod arrays. By optimizing the pore diameter and cell length of the AAO template as well as the RR-P3HT concentration and solvents to control the capillary force in the vacuum oven, RR-P3HT solutions were successfully filled into the AAO templates. After removal of the AAO template, RR-P3HT nanorod arrays with an average height of ~70 nm and width of ~55 nm were obtained. The results presented in this study may pave the way for facile modification of conjugated polymers for nanoscale devices such as solar cells and displays. Investigation into applications of the RR-P3HT nanorod array films to solid state solar cells with an extremely thin absorber layer are currently underway.

Experimental

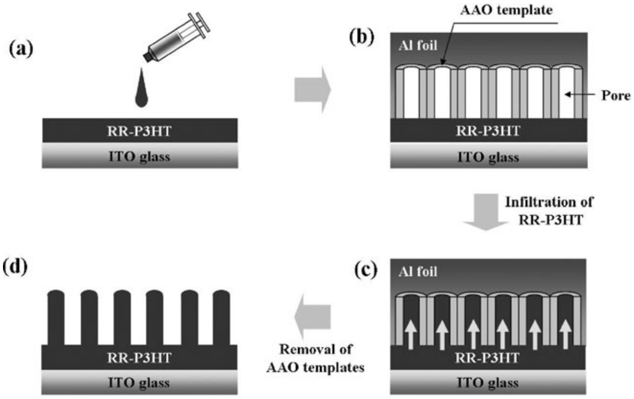
Materials

Aluminium foil (99.999%, 0.5 T) and chemical solvents were purchased from Goodfellow Cambridge Ltd. and Aldrich, respectively. RR-P3HT was obtained from Rieke Metals, Inc. (USA, regioregularity = 95.4%).[38,39] All chemicals were used as received. The ITO (10 Ω cm) substrate was obtained from Samsung Corning Co. (Korea). High purity water (Milli-Q, Millipore) was used for all experiments. The ITO substrate was washed with acetone, ethanol, and deionized water (18.2 MΩ cm) in an ultrasonication bath for 30 min followed by a final wash in isopropanol.

Preparation of AAO templates

The AAO templates were prepared as reported elsewhere.[40–43] In order to obtain well-aligned pore channels, the fabrication of the AAO template was carried out by a two step anodization method. For the 1st anodization of the aluminium, a constant voltage of 40 V was applied for about 12 h in a 0.3 M oxalic acid solution maintained at 0 °C. The grown alumina layer with pores was etched away in a mixed solution of phosphoric acid (6% H_3PO_4) and chromic acid (1.8% CrO_3) for about 12 h at 60 °C. To obtain regular arrays of nano-channels, the 2nd anodization was carried out under the same conditions as the 1st anodization. Then, the pores in the alumina were widened by etching in 0.1 M phosphoric acid. The AAO templates of hexagonal nano-channel arrays were realized through a self-assembling process during the anodization of aluminium. In general, cell lengths and pore diameters are controlled by the 2nd anodization time and the pore widening time, respectively.[40]

For one set of experiments, the 2nd anodization time was held constant at 30 min and the pore widening time was varied among 60, 75, 90, 105, and 120 min to determine the effect of pore diameter. In a separate set of experiments, the pore widening time was maintained at 1 h while the 2nd anodization time was varied among 2, 3, 5, 10, and 60 min to investigate the influence of the cell length.



Scheme 1 Schematic representation of RR-P3HT nanorod array formation on the ITO substrate with AAO templates and capillary force in a vacuum oven.

Formation of RR-P3HT nanorods using AAO templates by capillary force in a vacuum oven

Initially, RR-P3HT (2 w/v%, 0.6 ml) films on the ITO substrate were prepared by a drop-coating method. Then, AAO templates were attached on drop-coated RR-P3HT films on the ITO substrate. These samples were kept in a vacuum oven at 250 °C for 6 h in order to fill the melted polymer into the pores of the AAO template by capillary force (Scheme 1). After filling the pores of the AAO template by capillary force, the etching process to remove the AAO template followed. In our procedure, we used only NaOH for the etching process compared with the conventional method which uses both NaOH and mercury chloride ($HgCl_2$).[44,45] The RR-P3HT rods in the AAO template were immersed in a 3 M NaOH solution for 50 min to remove alumina between the Al foil and RR-P3HT nanorods. Al foil with an alumina layer was easily removed after 50 min from the RR-P3HT nanorods surface without additional $HgCl_2$ treatment. Then, the samples were once again soaked in a 3 M NaOH solution for 10 min to completely eliminate the remaining alumina particles. The surface morphology of the RR-P3HT nanorod arrays on the ITO substrate was measured using both a cold field-emission scanning electron microscope (Cold FE-SEM, Hitachi S-4800) and an Atomic Force Microscope (AFM, Digital Instruments, Tapping mode). The UV-visible absorption spectra were obtained using a Shimadzu UV-3600 spectrophotometer.

Acknowledgements

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Notes and references

1 A. Sun, J. W. Lauher and N. S. Goroff, *Science*, 2006, **312**, 1030.
2 S. H. Choi, B. S. Kim and C. D. Frisbie, *Science*, 2008, **320**, 1482.
3 J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222.

4 W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurisic, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak and W.-K. Chan, *Nat. Mater.*, 2007, **6**, 521.
5 F. Schindler, J. M. Lupton, J. Muller, J. Feldmann and U. Scherf, *Nat. Mater.*, 2006, **5**, 141.
6 I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 328.
7 D. J. Lipomi, R. C. Chiechi, M. C. Dickey and G. M. Whitesides, *Nano Lett.*, 2008, **8**, 2100.
8 A. A. R. Neves, A. Camposeo, R. Cingolani and D. Pisignano, *Adv. Funct. Mater.*, 2008, **18**, 751.
9 Y. Oaki and H. Imai, *Adv. Mater.*, 2006, **18**, 1807.
10 Y. Tian, C.-Y. Chen, M. A. Haller, N. M. Tucker, J.-W. Ka, J. Luo, S. Huang and A. K.-Y. Jen, *Macromolecules*, 2007, **40**, 97.
11 G. Lu, H. Tang, Y. Qu, L. Li and X. Yang, *Macromolecules*, 2007, **40**, 6579.
12 W. Niu, M. D. Smith and J. J. Lavigne, *J. Am. Chem. Soc.*, 2006, **128**, 16466.
13 D. J. D. Moet, L. J. A. Koster, B. d. Boer and P. W. M. Blom, *Chem. Mater.*, 2007, **19**, 5856.
14 D. Vak, S.-S. Kim, J. Jo, S.-H. Oh, S.-I. Na, J. Kim and D.-Y. Kim, *Appl. Phys. Lett.*, 2007, **91**, 081102.
15 X. Zhan, Z. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow, Y. Li, D. Zhn, B. Kippelen and S. R. Marder, *J. Am. Chem. Soc.*, 2007, **129**, 7246.
16 S. S. Williams, M. J. Hampton, V. Gowrishankar, I.-K. Ding, J. L. Templeton, E. T. Samulski, J. M. DeSimone and M. D. McGehee, *Chem. Mater.*, 2008, **20**, 5229.
17 G. Zhao, T. Ishizaka, H. Kasai, H. Oikawa and H. Nakanishi, *Chem. Mater.*, 2007, **19**, 1901.
18 B. Walker, A. Tamayo, J. Yang, J. Z. Brzezinski and T.-Q. Nguyen, *Appl. Phys. Lett.*, 2008, **93**, 063302.
19 J. Fang, Y. Yang and L. Edman, *Appl. Phys. Lett.*, 2008, **93**, 063503.
20 A. Haldi, B. Domercq, B. Kippelen, R. D. Hreha, J.-Y. Cho and S. R. Marder, *Appl. Phys. Lett.*, 2008, **92**, 253502.
21 D. H. Park, H. S. Kim, Y. B. Lee, J. M. Ko, J.-Y. Lee, H.-J. Kim, D.-C. Kim, J. Kim and J. Joo, *Synth. Met.*, 2008, **158**, 90.
22 M. Fu, Y. Zhn, R. Tan and G. Shi, *Adv. Mater.*, 2001, **13**, 1874.
23 J. Cao, J. Sun, G. Shi, H. Chen, Q. Zhang, D. Wang and M. Wang, *Mater. Chem. Phys.*, 2003, **82**, 44.
24 Z. Cai and C. R. Martin, *J. Am. Chem. Soc.*, 1989, **111**, 4138.
25 M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater.*, 2005, **4**, 455.
26 P. A. Du, H. H. Chen and Y. C. Lu, *Appl. Phys. Lett.*, 2006, **89**, 253513.
27 W. Lee, S. H. Kang, S. K. Min, Y.-E. Sung and S.-H. Han, *Electrochem. Commun.*, 2008, **10**, 1579.
28 D. H. Park, B. H. Kim, M. G. Jang, K. Y. Bae and J. Joo, *Appl. Phys. Lett.*, 2005, **86**, 113116.
29 H.-J. Kim, D.-C. Kim, R. Kim, D.-H. Park, H.-S. Kim, J. Joo, Y. D. Suh and J. Kim, *J. Appl. Phys.*, 2007, **101**, 053514.
30 M. A-Ibrahima, O. Ambacher, S. Sensfuss and G. Gobsch, *Appl. Phys. Lett.*, 2005, **86**, 201120.
31 J.-F. Chang, B. Sun, D. W. Breiby, M. M. Nielsen, T. I. Solling, M. Giles, I. McCulloch and H. Sirringhaus, *Chem. Mater.*, 2004, **16**, 4772.
32 W. Lee, S. Shin, S.-H. Han and B. W. Cho, *Appl. Phys. Lett.*, 2008, **92**, 193307.
33 W. Lee, S.-K. Min, S. Shin, S.-H. Han and S.-H. Lee, *Appl. Phys. Lett.*, 2008, **92**, 023507.
34 J. Park, S.-H. Han, S. Senthilarasu and S.-H. Lee, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 751.
35 J.-C. Li, H.-Y. Lee, S.-H. Lee, K. Zong, S.-H. Jin and Y.-S. Lee, *Synth. Met.*, 2008, DOI: 10.1016/j.synthmet.2008.08.016.
36 *An Introduction To Fluid Dynamics*, ed. G. K. Batchelor, Cambridge University Press, Cambridge, 1967, ch. 1, pp. 60–69.
37 Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha and M. Ree, *Nat. Mater.*, 2006, **5**, 197.
38 M. C. Gallazzi, L. Castellani, G. Zerbi and P. Sozzani, *Synth. Met.*, 1991, **41–43**, 495.
39 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.
40 J. W. Diggle, T. C. Downie and C. W. Goulding, *Chem. Rev.*, 1969, **69**, 365.
41 K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn and U. Golsele, *Nano Lett.*, 2002, **2**, 677.
42 T. X. Terry, D. P. Richard and S. R. Rodney, *Langmuir*, 2003, **19**, 1443.
43 C. Kim, J.-B. Park, H.-G. Jee, S.-B. Lee, J.-H. Boo, S.-K. Kim, J.-B. Yoo, J.-S. Lee and H. Lee, *J. Nanosci. Nanotechnol.*, 2005, **5**, 306.
44 C. Guofang, A. S. Steven and L. M. Robin, *Langmuir*, 2007, **23**, 11777.
45 C.-C. Wang, Q.-D. Shen, S.-C. Tang, Q. Wu, H.-M. Bao, C.-Z. Yang and X.-Q. Jiang, *Macromol. Rapid Commun.*, 2008, **29**, 724.