

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263200376>

Enhanced Vertical Concentration Gradient in Rubbed P₃HT:PCBM Graded Bilayer Solar Cells

ARTICLE in JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JULY 2012

Impact Factor: 7.46 · DOI: 10.1021/jz300710a

CITATIONS

25

READS

49

6 AUTHORS, INCLUDING:



[Gianmichele Arrighetti](#)

Italian National Research Council

33 PUBLICATIONS 557 CITATIONS

SEE PROFILE



[Luisa Barba](#)

Italian National Research Council

60 PUBLICATIONS 987 CITATIONS

SEE PROFILE



[W. Porzio](#)

Italian National Research Council

229 PUBLICATIONS 3,033 CITATIONS

SEE PROFILE



[Hideyuki Murata](#)

Japan Advanced Institute of Science and Tech...

152 PUBLICATIONS 4,271 CITATIONS

SEE PROFILE

Enhanced Vertical Concentration Gradient in Rubbed P3HT:PCBM Graded Bilayer Solar Cells

Varun Vohra,^{*,†} Gianmichele Arrighetti,[‡] Luisa Barba,[‡] Koichi Higashimine,[†] William Porzio,[§] and Hideyuki Murata^{*,†}

[†]Japan Advanced Institute of Science and Technology (JAIST), School of Materials Science, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

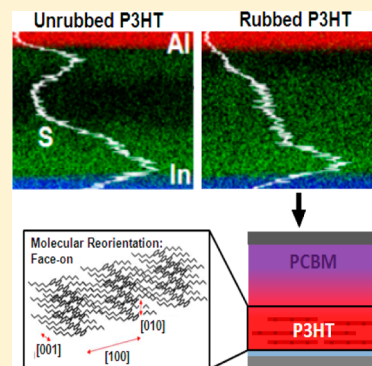
[‡]Istituto di Cristallografia del CNR - c/o Sincrotrone Elettra, Strada Statale 14-Km 163,5 Area Science Park, 34012 Basovizza, Trieste, Italy

[§]Istituto per lo Studio delle Macromolecole (ISMAL) Via Bassini, 15, Milano, 20133, Italy

Supporting Information

ABSTRACT: Graded bilayer solar cells have proven to be at least as efficient as the bulk heterojunctions when it comes to the Poly(3-hexylthiophene) (P3HT) - [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) donor–acceptor system. However, control of the vertical concentration gradient using simple techniques has never been reported. We demonstrate that rubbing the P3HT layer prior to PCBM deposition induces major morphological changes in the active layer. Using the newly introduced energy-dispersive X-ray spectroscopy element mapping technique, we found that rubbing P3HT induces the formation of an ideal vertical donor–acceptor concentration gradient. Furthermore, the P3HT crystallites undergo a molecular reorientation from edge-on to face-on configuration inducing a better charge transport in the vertical direction. The combination of these two major morphological changes leads to the fabrication of high-performance solar cells that exhibit, to date, the record efficiencies for spin-coated graded bilayers solar cells.

SECTION: Energy Conversion and Storage; Energy and Charge Transport



In recent years, graded bilayer poly(3-hexylthiophene) (P3HT) - [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) solar cells have been introduced as an alternative to bulk heterojunctions with average efficiencies reaching up to 3.5%.^{1–3} This method, based on selecting a pair of solvents to spin-coat PCBM on top of a thin P3HT layer, allows for PCBM molecules to diffuse inside the P3HT network without entirely dissolving the bottom layer. Although this type of active layer has a great potential as it creates a donor–acceptor concentration gradient, not much attention has been given to improve further the performances through simple process methods. Among simple methods, rubbing, well-established for liquid-crystal display technology,^{4,5} has recently shown positive results. It may, for instance, induce molecular orientation leading to improved charge injection/blocking properties in rubbed films⁶ and shows interesting results in organic light-emitting devices,⁷ field-effect transistors,^{8,9} and solar cells.^{10–12}

Recently, rubbed bulk heterojunctions and inverted solar cells have been used as polarizers in solar-cell liquid-crystal displays.^{10–12} Previous studies have demonstrated that extensive rubbing provides chain orientation along the rubbing axis. After rubbing up to 80 times, an orientation of the absorption dipole moment of the polymer can be observed, and the devices fabricated using rubbed active layers can consequently act as polarizer and solar cells simultaneously.

However, the devices prepared using rubbing do not display any enhanced photovoltaic properties.

In the present Letter, we focus on the increase in performances of graded bilayer solar cells upon rubbing. Unlike previous works on rubbed P3HT-PCBM solar cells,^{10–12} we demonstrate that rubbing induces an improvement in device performances related to two key factors: the formation of a better donor–acceptor vertical gradient within the active layer and the reorientation of the P3HT molecules from edge-on to face-on configuration within the thin active layer. Both of these effects lead to enhanced fill factors (FF) and photovoltaic properties. Using this simple method, we fabricate devices that exhibit a maximum power conversion efficiency (PCE) of 3.99% (average PCE over 16 devices of 3.81%), which overcomes the device performances previously reported as the most efficient spin-coated bilayers.³

We first investigate the influence of rubbing P3HT layer on the device performances. P3HT is spin-coated on top of indium tin oxide (ITO) substrates covered by 35 nm of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Figure 1a). P3HT thin films are rubbed 0, 3, 5,

Received: May 31, 2012

Accepted: June 18, 2012

Published: June 18, 2012

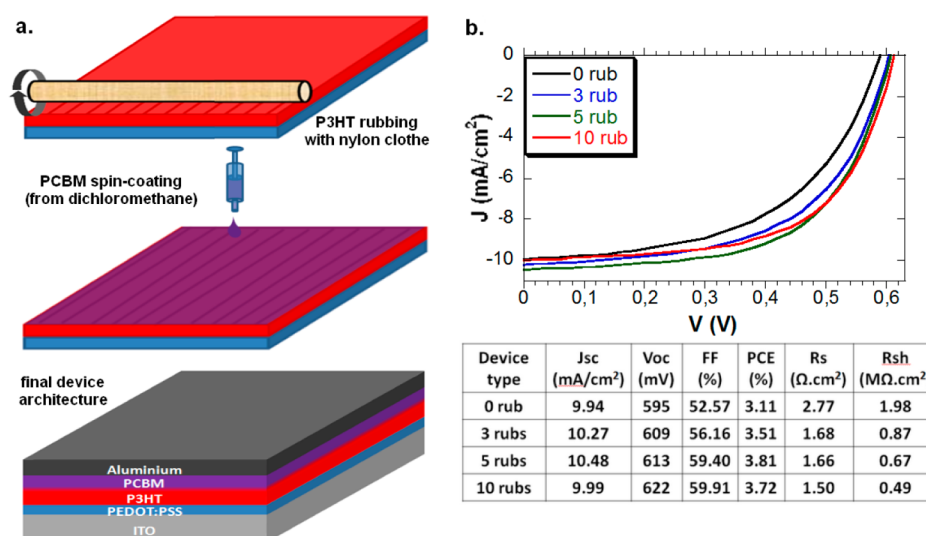


Figure 1. (a) Schematic representation of the step-by-step preparation of P3HT rubbed with nylon clothes devices. (b) Characteristics and J–V curves of devices prepared with 0, 3, 5, and 10 rubs (annealed at 140 °C for 10 min, average of 16 devices).

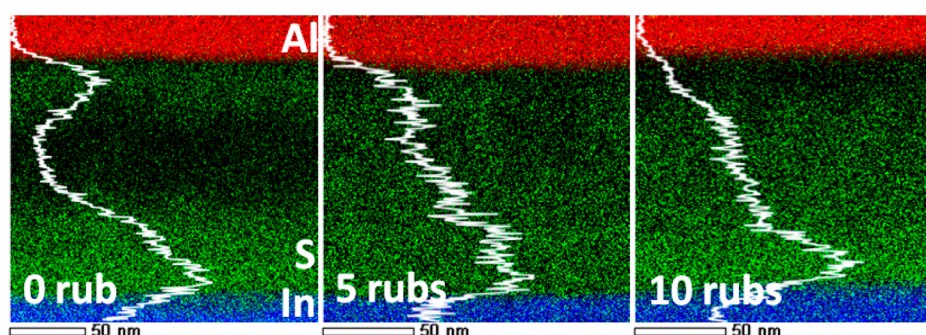


Figure 2. EDS element mapping and plots (white line) of sulfur counts along the cross section of devices obtained after rubbing the P3HT layer 0, 5, and 10 times. The detected elements are aluminum (red), sulfur (green), and indium (blue).

and 10 times prior to PCBM deposition from dichloromethane solution, and devices are finalized using aluminum as the top electrode.

Upon rubbing, all Jsc (short circuit current), Voc (open circuit voltage), FF, and PCE increase (highest performing device, five times rubbed P3HT, Jsc = 10.3 mA/cm², Voc = 626 mV, FF = 60.7%, PCE = 3.99%). Both the Voc and the FF improve with increasing rubbing (Figure 1c). Voc is found to be related directly to the changes in the HOMO level of the P3HT. HOMO levels measured by photoelectron yield spectroscopy (PYS) on the P3HT films prior to PCBM deposition (Figure SI1 of the Supporting Information) give energies of 4.81, 4.99, 5.04, and 5.11 eV for the samples rubbed 0, 3, 5, and 10 times, respectively. The differences in measured energy levels correspond almost exactly to the increase observed in Voc. Molecular reorientation at the donor–acceptor interface in organic solar cells has been proven to influence greatly the resulting photovoltaic performances, and, more specifically, such molecular reorientation can induce a control over the Voc⁶ similar to the one observed in the rubbed P3HT devices. In the last part of this work, we will investigate whether such reorientation can be found in rubbed P3HT films using grazing incident X-ray diffraction (GI-XRD).

Atomic force microscopy (AFM) images (Figure SI2 of the Supporting Information) reveal that up to 5-times rubbing, gratings are created on the surface of the P3HT layer, which

then disappear when increasing the rubbing number to 10 times. We will therefore focus on understanding the differences between unrubbed and 5- and 10-times rubbed devices.

As in graded bilayers the vertical concentration gradient greatly influences the FF, we investigate the P3HT location within the active layer cross section (Figure 2) using energy-dispersive X-ray spectroscopy (EDS) element mapping. After PCBM spin-coating, high P3HT concentrations are found close to PEDOT:PSS and aluminum for unrubbed films, leaving most of the PCBM trapped between two electron blocking layers. During PCBM deposition, a small amount of P3HT is dissolved, leading to the formation of such sandwiched layers.

To evaluate the interactions between unrubbed and rubbed P3HT, PCBM, and dichloromethane, we calculate their surface tensions through contact angle measurements (with water and ethylene glycol). We compare the unrubbed and 10-times rubbed films as they have similar surface roughness (Table SI1 of the Supporting Information). As P3HT is apolar, we use the dispersive surface energy components for more reliable comparison. We obtain 25.1, 23.0, 26.5, and 11.1 mJ/m² for unrubbed, 10-times rubbed P3HT, dichloromethane, and PCBM, respectively, confirming that the rubbed P3HT is more resistant to dichloromethane and more compatible with PCBM, allowing for a better diffusion of PCBM into rubbed P3HT while decreasing the amount of P3HT dissolved during the process. Therefore, as observed in Figure 2, upon rubbing,

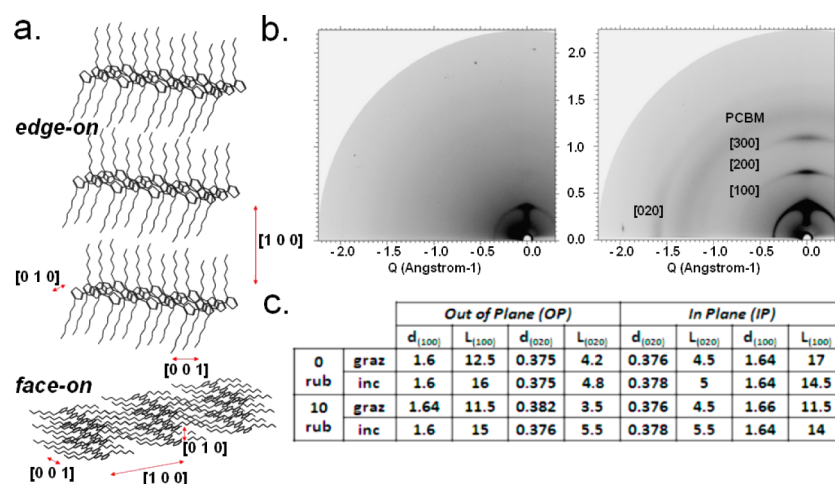


Figure 3. (a) Edge-on and face-on configurations of P3HT. (b) Typical grazing (left) and incident (right) XRD obtained for rubbed active layers and (c) summary of the XRD measurements (d and L in nanometers, details in the Supporting Information).

the P3HT in contact with aluminum gradually disappears, which induces a decrease in series resistance of the devices (R_s) and explains the high FF of rubbed devices.

Moreover, P3HT crystallinity and crystallites orientation in the active layer further influence the device performances. Figure 3 summarizes the orientation of the macromolecules observed by GI-XRD after deposition of PCBM. The main features here detected are consistently in agreement with the recent papers on P3HT-PCBM system¹³ and P3HT rubbed films.¹⁴ The comparison with the latter is weakened by the different kind of films (P3HT-PCBM compared with P3HT alone), whereas the former focuses on blends of the two materials (deposited simultaneously). Typical 2D images show three orders of $[1\ 0\ 0]$ direction, the $(0\ 2\ 0)$ reflection ($q = 1.63\ \text{\AA}^{-1}$), and the bump at $0.45\ \text{nm}$ ($q = 1.39\ \text{\AA}^{-1}$). The spots are readily assigned to crystalline P3HT, whereas the amorphous halo is attributed to PCBM because the amorphous SiOx and PEDOT:PSS, usually centered at $0.41\ \text{nm}$ ($q = 1.53\ \text{\AA}^{-1}$), are hidden by film thickness. Out-of-plane (OP) (100) and in-plane (IP) (020) provide information about the average dimensions of the edge-on crystallites, whereas OP (020) and IP (100) relate the dimensions of the face-on crystallites. Grazing (graz) and incident (inc) diffraction measurements, respectively, probe the surface (5 nm of depth) and the whole film.

To understand the influence of rubbing on the P3HT films at the molecular level and avoid misunderstandings related to gratings formed in the 5-times rubbed films, we compare the two extreme cases of unrubbed and 10-times rubbed active layers (details of GI-XRD measurements for 5-times rubbed films in the Supporting Information). In unrubbed P3HT:PCBM graded bilayers, P3HT crystallites are detected in the top 5 nm (in agreement with EDS data). These crystallites, detected at the top of the unrubbed active layer (grazing measurement), which originate from small amounts of P3HT dissolved during the PCBM spin-coating process, are mainly in face-on configuration whereas in the bulk (incident measurement), we observe a much lower face-on to edge-on crystallites ratio, which demonstrates that the P3HT crystallites in the lower part of the active layer (close to PEDOT:PSS) are mainly in edge-on configuration. Upon rubbing, the crystallinity of the active layer (incident measurement) increases, making the rubbed films more resistant to dichloromethane (in

agreement with surface tension calculations). Consequently, the amount of face-on crystallites found at the top of the active layer is significantly reduced, confirming that the P3HT in contact with the aluminum electrode gradually disappears upon rubbing. (A smaller amount of P3HT is dissolved during the PCBM spin-coating process.)

To analyze the changes in orientation of the crystallites upon rubbing, we compare the bulk measurements of the unrubbed and 10-times rubbed films. In the 10-times rubbed films, both the crystallinity and the face-on to edge-on increase as compared with the unrubbed film. Therefore, GI-XRD results confirm not only that the P3HT in contact with the aluminum electrode gradually disappears but also that upon rubbing some molecular reorientation from edge-on to face-on configuration occurs, leading to a better vertical charge transport in the devices.

In summary, with a simple technique, we can obtain P3HT:PCBM bilayer solar cells with enhanced photovoltaic properties. The devices based on the 5-times rubbed P3HT thin films display an average PCE of 3.81% that corresponds to a new record for the graded bilayer P3HT:PCBM devices. The highest performing device exhibits a J_{sc} of $10.3\ \text{mA}/\text{cm}^2$, a V_{oc} of 626 mV, an FF of 60.7%, and a PCE of 3.99%. These remarkable increases in FF are related to the formation of ideal vertical concentration gradients due to the increase in crystallinity and changes in surface tension of the molecular reoriented rubbed P3HT films. Because the rubbing technique is very well known in the industrial world, the work here introduced is a very attractive and promising first step to making commercially available enhanced-efficiency solar cells based on well-known materials.

EXPERIMENTAL SECTION

P3HT solutions ($30\ \text{mg}\cdot\text{mL}^{-1}$ in chlorobenzene) are spin-coated at 2500 rpm on 35 nm thick PEDOT:PSS layers to produce 80 nm thin films. The rubbing process is done with a nylon cloth following one direction. The unrubbed and rubbed P3HT are then covered with a solution of PCBM ($10\ \text{mg}\cdot\text{mL}^{-1}$ in dichloromethane, 4000 rpm for 10s). Devices are finalized by evaporating a 100 nm thick aluminum cathode under vacuum (10^{-6} Torr) and annealed ($140\ ^\circ\text{C}$ for 10 min) after encapsulation with a glass cap using an ultraviolet curing

epoxy resin inside a nitrogen-filled glovebox. The active area of the devices was defined to 2 mm².

GI-XRD has been carried out at 25 °C at the XRD1 beamline of the ELETTRA synchrotron facility (Trieste, Italy) using 10.34 keV energy (0.12 nm). EDS for elemental analysis was carried out with a scanning transmission electron microscope, JEM-ARM200F from JEOL.

Further details of characterization methods and materials are in the Supporting Information.

■ ASSOCIATED CONTENT

● Supporting Information

PYS, AFM complete GI-XRD characterization of the rubbed and unrubbed films of P3HT, EDS element mapping of thinner rubbed active layers, and experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: varunvohra1984@gmail.com (V.V.); murata-h@jaist.ac.jp (H.M.). Tel: +81-761-51-1531. Fax: +81-761-51-1532.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval of the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (no. 20108012, “pi-Space”) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. V.V. would like to acknowledge greatly financial support through research fellowships from the Japan Society for Promotion of Science for postdoctoral fellowships for foreign researchers.

■ REFERENCES

- (1) Wang, D. H.; Lee, H. K.; Choi, D.-G.; Park, J. H.; Park, O. O. Solution-Processable Polymer Solar Cells from a Poly(3-hexylthiophene)/[6,6]-phenyl C61-butyric Acidmethyl Ester Concentration Graded Bilayers. *Appl. Phys. Lett.* **2009**, *95*, 043505.
- (2) Ayzner, A. L.; Tassone, C. J.; Tolbert, S. H.; Schwartz, B. J. Reappraising the Need for Bulk Heterojunctions in Polymer–Fullerene Photovoltaics: The Role of Carrier Transport in All-Solution-Processed P3HT/PCBM Bilayer Solar Cells. *J. Phys. Chem. C* **2009**, *113*, 20050–20060.
- (3) Lee, K. H.; Schwenn, P. E.; Smith, A. R. G.; Cavaye, H.; Shaw, P. E.; James, M.; Krueger, K. B.; Gentle, I. R.; Meredith, P.; Burn, P. Morphology of All-Solution-Processed “Bilayer” Organic Solar Cells. *Adv. Mater.* **2011**, *23*, 766–770.
- (4) Wu, H.-M.; Tang, J.-H.; Luo, Q.; Zhu, Z.-M.; Lu, Z.-H.; Wei, Y. Liquid-Crystal Alignment of Rubbed Polyimide Films: A Microscopic Investigation. *Appl. Phys. B: Laser Opt.* **1996**, *62*, 613–618.
- (5) Yang, F.; Zorinians, G.; Ruan, L.; Sambles, J. R. Optical Anisotropy and Liquid-Crystal Alignment Properties of Rubbed Polyimide Layers. *Liq. Cryst.* **2007**, *34*, 1433–1441.
- (6) Duhm, S.; Heime, G.; Salzmänn, I.; Glowatzki, H.; Johnson, R. L.; Vollmer, A.; Rabe, J. P.; Koch, N. Orientation-Dependent Ionization Energies and Interface Dipoles in Ordered Molecular Assemblies. *Nat. Mater.* **2008**, *7*, 326–332.
- (7) Matsushima, T.; Murata, H. Enhanced Charge-Carrier Injection Caused by Molecular Orientation. *Appl. Phys. Lett.* **2011**, *98*, 253307.
- (8) Derue, G.; Serban, D. A.; Leclerc, P.; Melinte, S.; Daman, P.; Lazzaroni, R. Controlled Nanorubbing of Polythiophene Thin Films for Field-Effect Transistors. *Org. Electron.* **2008**, *9*, 821–828.
- (9) Abbas, M.; D’Amico, F.; Ali, M.; Mencarelli, I.; Setti, L.; Bontempi, E.; Grunnella, R. Rubbing Effects on the Structural and Optical Properties of Poly(3-hexylthiophene) Films. *J. Phys. D: Appl. Phys.* **2010**, *43*, 035103.
- (10) Zhu, R.; Kumar, A.; Yang, Y. Polarizing Organic Photovoltaics. *Adv. Mater.* **2011**, *23*, 4193–4198.
- (11) Park, B.; Huh, Y. H.; Shin, J. C. In-Plane Anisotropy of Photovoltaic Effects in Aligned Polymer Solar Cells. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 3543–3549.
- (12) Huh, Y. H.; Shin, J. C.; Kim, Y. C.; Park, B. Reflective Type Solar-LCDs by Using Polarizing Polymer Solar Cells. *Opt. Express* **2012**, *20*, A278–A286.
- (13) Lilliu, S.; Agostinelli, T.; Pires, E.; Hampton, M.; Nelson, J.; Macdonald, J. M. Dynamics of Crystallization and Disorder during Annealing of P3HT/PCBM Bulk Heterojunctions. *Macromolecules* **2011**, *44*, 2725–2734.
- (14) Hartmann, L.; Tremel, K.; Uttiya, S.; Crossland, E.; Ludwigs, S.; Kayunkid, N.; Vergnat, C.; Brinkmann, M. 2D Versus 3D Crystalline Order in Thin Films of Regioregular Poly(3-hexylthiophene) Oriented by Mechanical Rubbing and Epitaxy. *Adv. Funct. Mater.* **2011**, *21*, 4047–4057.