



Polymer Photovoltaic Cells

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World Energy Supply and Demand

International Energy Agency best estimate for energy supply in 2030

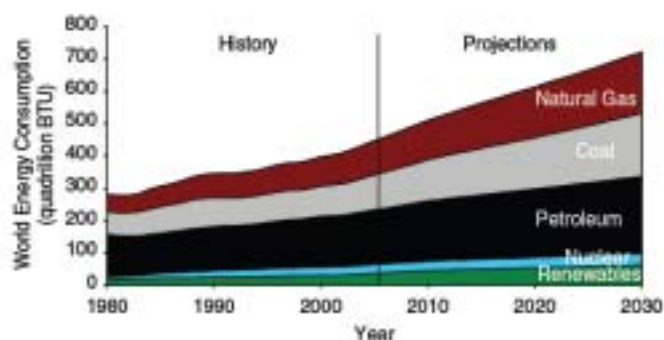


Table 1: Current Sources for World Energy Supply.

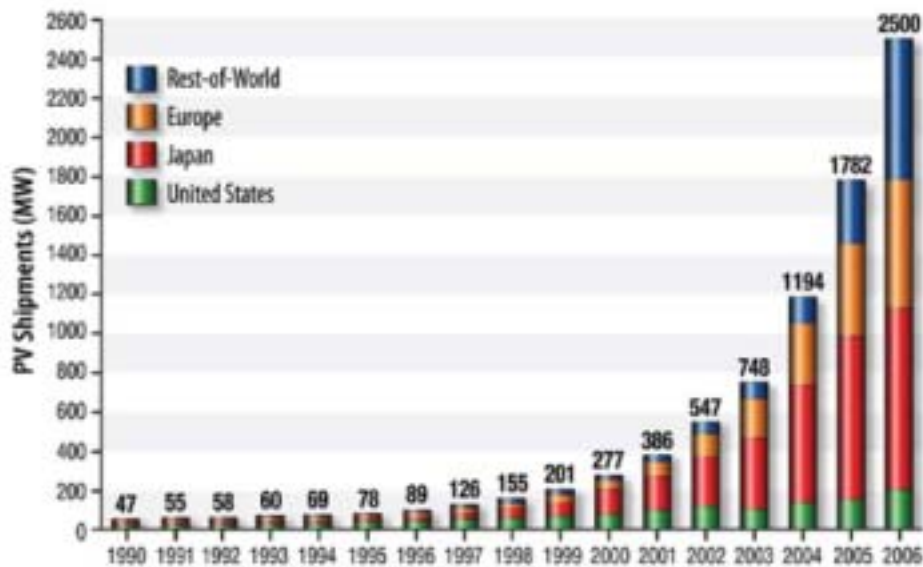
Energy Source	Supply Percentage in 2005
Oil	38
Natural gas	23
Coal	23
Nuclear	7
Renewable	9

MRS Bulletin, 33(4), April 2008



How about Solar Energy?

World photovoltaic module production (in megawatts), total consumer, and commercial per country



Most of this production is from crystalline or multicrystalline Si solar cell at present.

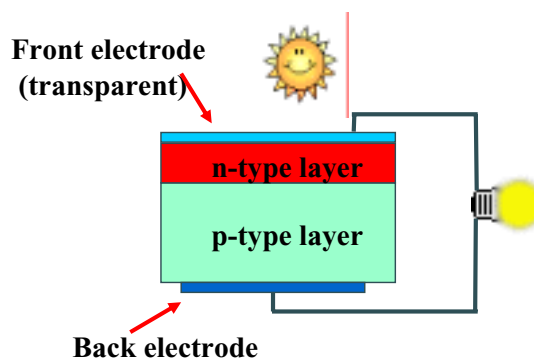


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Photovoltaic (PV) Device

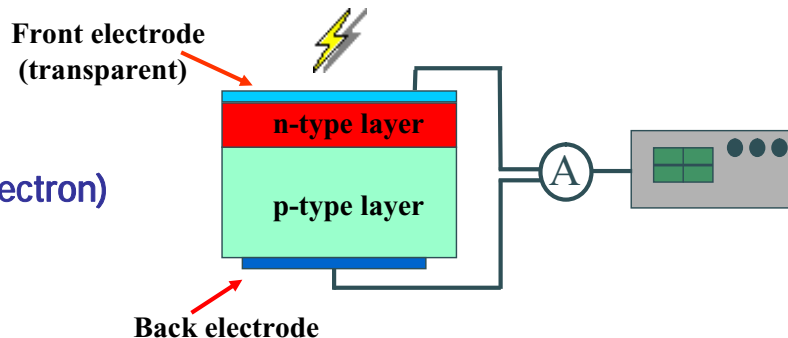
Solar cell

Produce electrical energy
Power conversion efficiency



Photodetector

Measure/detect light
Quantum yield
(conversion of photon to electron)
additional external field
improve detection limit




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Outline


Inorganic Materials

- Thick Crystalline Materials
- Crystalline Silicon
 - Single-crystal
 - Multicrystalline
- Gallium Arsenide (GaAs)



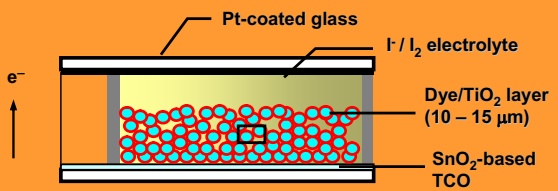
Inorganic Materials

- Thin Film Materials
- Amorphous Silicon (a-Si)
- Cadmium Telluride (CdTe)
- Copper Indium Diselenide (CuInSe₂, or CIS)



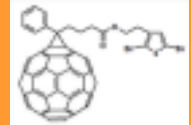
Solar Cell

Dye-Sensitized Solar Cells



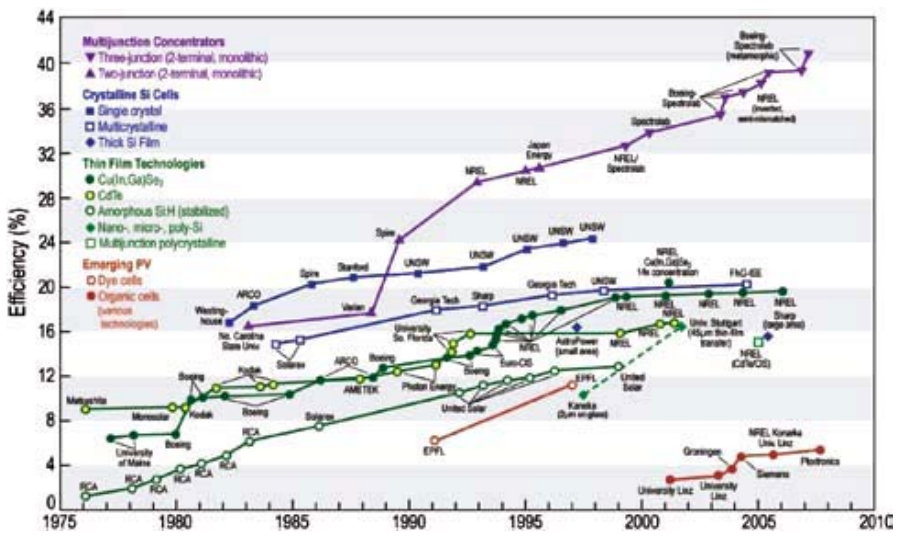
Organic Materials

- Pure and chemically modified fullerenes
- Polythiophene derivatives
- Polyphenylene vinylene



Cell Efficiency

Progress of research-scale photovoltaic device efficiencies



Silicon Solar Cell

► Crystalline Silicon Solar Cells

- Single crystal & Polycrystalline
- High efficiency, but high cost
- the thickness of crystalline solar cell: 0.3~0.5mm
 - : to satisfy the mechanical strength
 - : to absorb sufficiently the exposed light onto the surface of the cell
- Efficiency: 24% (single crystal) 18% (polycrystalline)



Single crystal & Polycrystal Silicon Solar Cells

► Amorphous Silicon Solar Cells

- Fabrication of Silicon layer onto the substrate by injection of SiH₄ gas at high voltage
- Simple method & very low cost (compared to crystalline silicon solar cell)
- Any size and shape is possible → the cells can be arranged compactly in the panel.
- The efficiency is decreased with time. (Intrinsic degradation)
- Efficiency: 10 – 12%

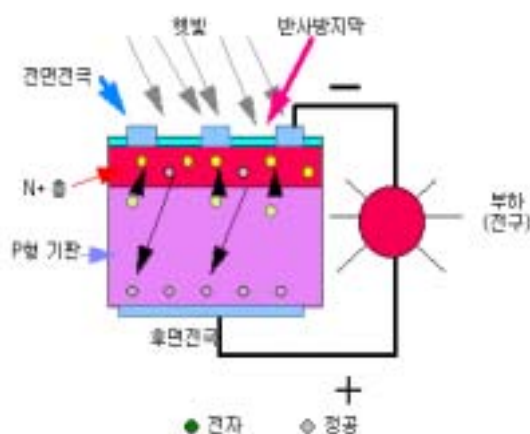


Amorphous Silicon Solar Cell

► a-Si/poly-Si Laminated Solar Cells

- the upper layer: amorphous Si layer
- the lower layer: polycrystalline Si layer or wafer (high absorbance of the light in the long wave length)
- Stable & high efficiency
- Efficiency : 10 ~ 13%

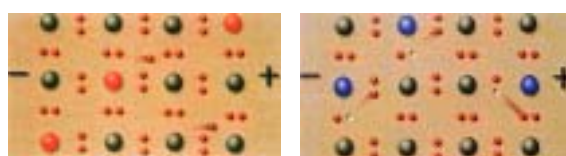
Typical Inorganic Solar Cell



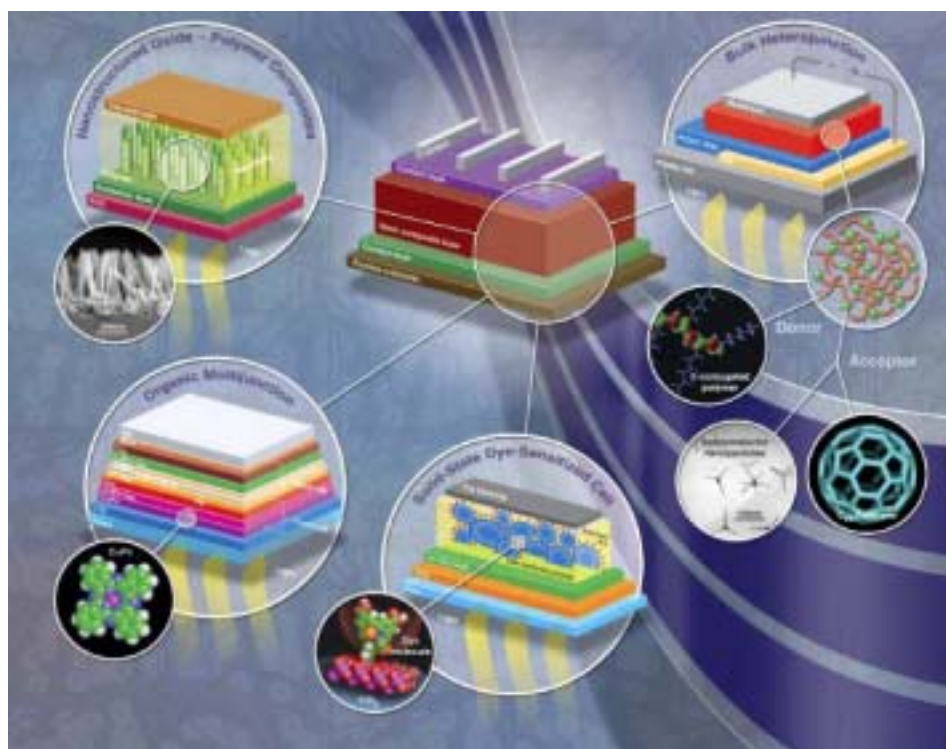
The front side: arsenic (As) with a small amount : **N type**
 The back side: boron (B) with μm thickness : **P type**

► This PN junction structure made the state that electron can be transported easily.

If the photons (the light of solar energy) expose in PN junction layer, positive charge and negative charge are generated by electron transporting. At this state, negative charge is transported to N type material and positive charge is moved to P type material. Therefore, potential difference (voltage) occurs and the current can be flowed.



Organic-Based Photovoltaics



MRS Bulletin, 30(1), January 2005

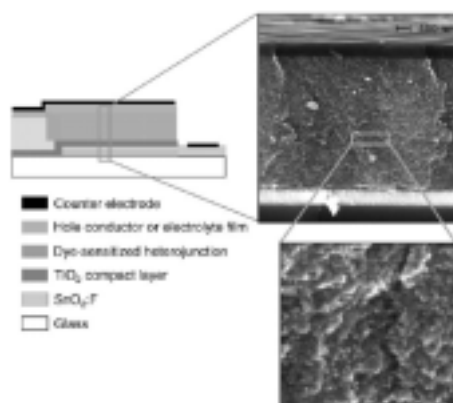
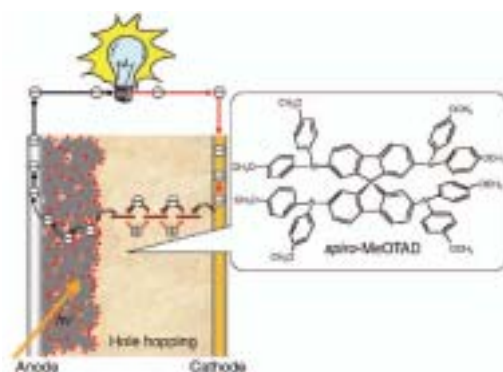


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Organic-Based Photovoltaics

Organic-Based Photovoltaics

1) Dye-sensitized Solar Cell



1. R.H. Friend and coworkers, *Nature* 376, 498 (1995)
2. M. Grätzel and coworkers, *Nature* 395, 583 (1998)
3. M. Grätzel and coworkers, *Nature Mater.* 2, 402 (2003)

► Dye-sensitized nanostructured oxide cells.

: These cells use an organic dye to absorb light and rapidly inject electrons into a nanostructured oxide such as anatase TiO_2 . The hole is scavenged by a redox couple, such as iodide/triiodide (I^-/I_3^-) in solution or by a solid-state organic semiconductor or ionic medium.

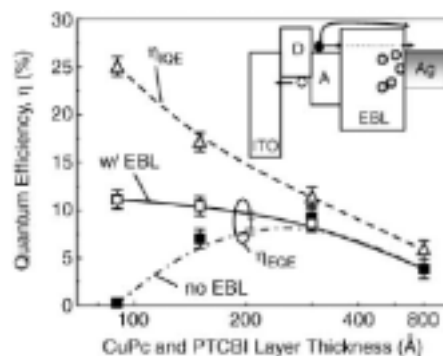
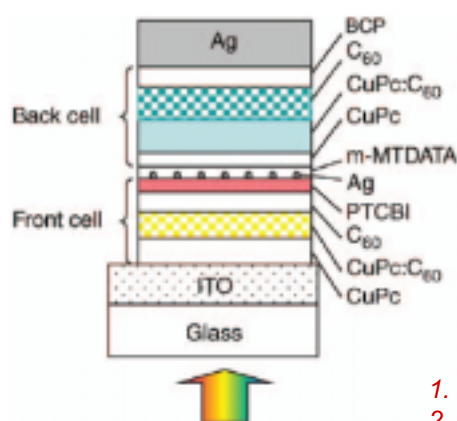
To date, the solid-state approaches have not been as effective, but progress is being made in understanding the nature of the redox behavior of the organic hole transporter. These approaches are discussed in many papers by Grätzel.



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Organic-Based Photovoltaics

2) Multilayer Devices using Small Molecule



1. C.W. Tang, *Appl. Phys. Lett.* 48, 183 (1986)

2. P. Peumans, S. Uchida, and S.R. Forrest, *Nature* 425, 158 (2003)

3. S.R. Forrest and coworkers, *Appl. Phys. Lett.* 86, 5757 (2005)

► **Multilayer devices in which small molecule organic solar cells are deposited sequentially to form a stacked device.**

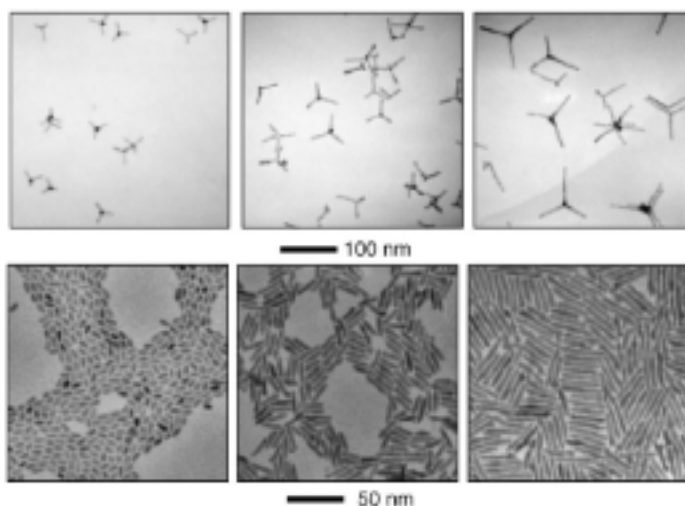
Recent progress in the reduction of the series resistance has led to increased efficiencies. This technology has the added benefit that multijunction tandem devices, which trade off current for voltage and possess higher theoretical efficiencies, can be fabricated in a straightforward manner.



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Organic-Based Photovoltaics

3) Organic-Inorganic Hybrid Solar Cell



1. A. P. Alivisatos and Coworkers, *Science* 295, 2425 (2002)

2. B.E. Sun, E. Marx, and N.C. Greenham,

Nano Lett. 3, 961 (2003)

3. A. P. Alivisatos and Coworkers, *Nano Lett.*, 7, 409 (2007)

► **Organic-inorganic composites consisting of nanocrystals of conventional semiconductors, such as CdSe, blended into a conjugated polymer matrix.**

In this case, both components can efficiently absorb light, and the bandgap of the nanocrystals can be tuned by growing them to different sizes.

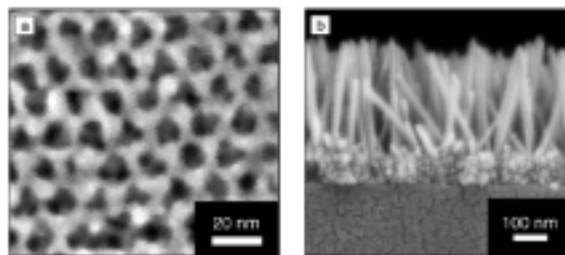
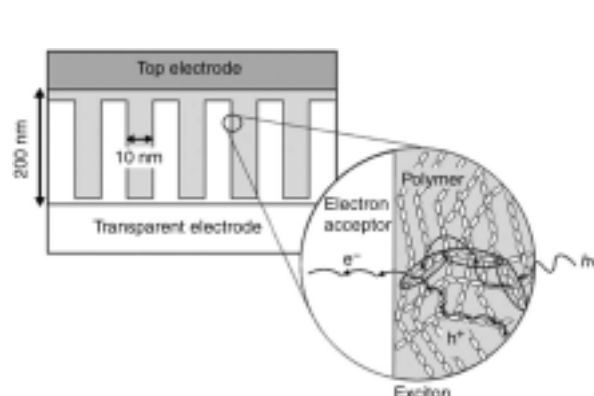
The energetics of the organic-inorganic interface is crucial. Recent progress in this area is led by Alivisatos group



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Organic-Based Photovoltaics

4) Ordered Organic–Inorganic Bulk Heterojunction Solar Cells



1. M.T. Anderson and coworkers, *Nature* 389, 364 (1997)
2. M.D. McGehee, and coworkers, *Adv. Funct. Mater.* 13, 301 (2003)
3. K.M. Coakley and M.D. McGehee, *Appl. Phys. Lett.* 83, 3380 (2003)

► **Organic–inorganic composites that combine a light-absorbing conjugated polymer as the donor and hole transporter with a nanostructured, large-bandgap inorganic semiconductor such as TiO_2 or ZnO as the acceptor and electron transporter.**

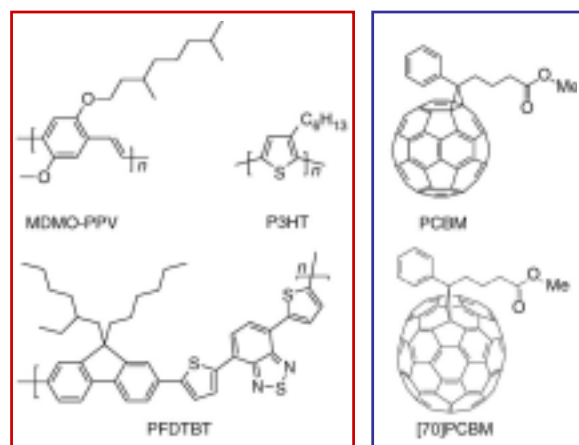
These work similarly to the bulk heterojunctions; however, the gross morphology of the mixture is determined by that of the nanostructured oxide that is grown in a self-organizing manner on the electrode. Optimization of the organic–inorganic interface is critical for these device..



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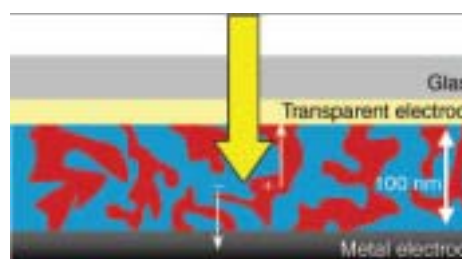
Organic-Based Photovoltaics

5) Polymer–Fullerene Bulk Heterojunction Solar Cells



Donor

Acceptor



1. N.S. Sariciftci and coworkers, *Appl. Phys. Lett.* 78, 841 (2001)
2. N.S. Sariciftci, *Adv. Funct. Mater.* 13, 85 (2003)
3. R.A.J. Janssen and coworkers, *Adv. Funct. Mater.* 14, 425 (2004)

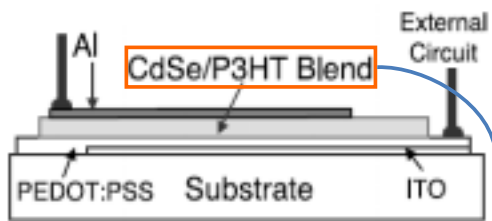
► **Organic–organic composites in which donor and acceptor species, which function as the hole and electron transporters, respectively, are intimately mixed to produce a “bulk heterojunction.”**

Among the most successful bulk heterojunction devices to date are consisted of a conjugated polymer such as poly(3-hexylthiophene) as the donor and a fullerene derivative as the acceptor. These devices are introduced by Sariciftci and Heeger.



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Organic-Inorganic Hybrid Solar Cell



**A. P. Alivisatos and Coworkers,
Science 295, 2425 (2002)**

1. Advantage of CdSe

: Inorganic semiconductors have a **good absorption coefficient of the solar spectrum**.

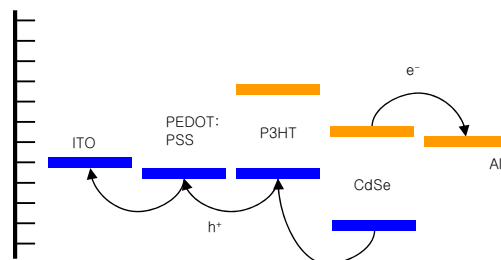
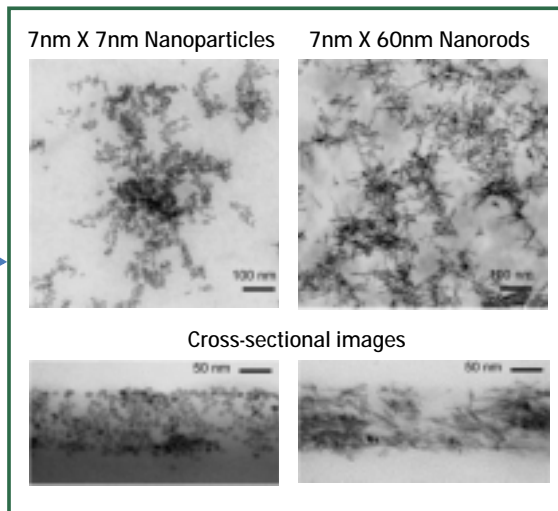
(Band gap of CdSe ~ 1.7eV)

2. Why Hybrid?

: Exciton dissociations occur at the interface between two materials. **The high electron affinity and electron mobility of CdSe and relatively low ionization potential P3HT that make charge separation easy.**

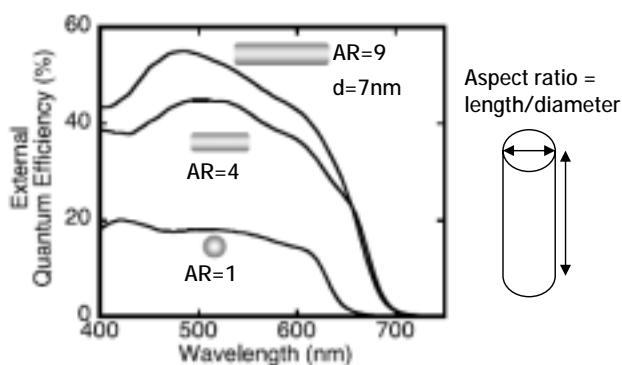
3. Why Nanostructure?

: Diffusion distances of excitations are ~10-15nm due to its low electron mobilities. -> efficient devices need to be very thin and nanostructured interface.



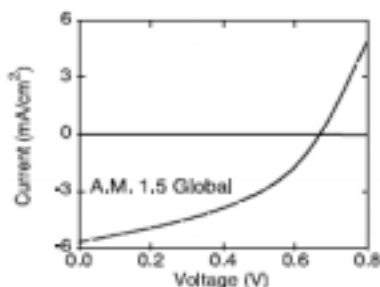
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Organic-Inorganic Hybrid Solar Cell

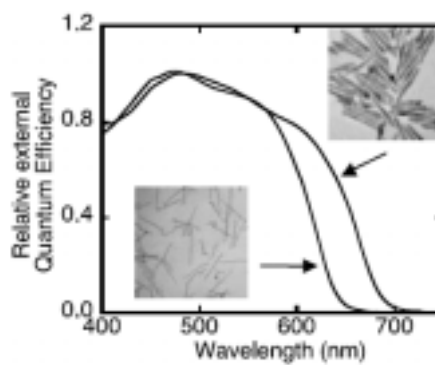


Aspect Ratio \propto External Quantum Efficiency

- Pathways of electrons
- Small number of interparticle hops of electrons



► With CdSe nanorods 7 nm
Power Conversion Efficiency = 1.7%
Under A.M. 1.5 Global solar conditions



Altering the diameter of the nanorods

Tuning the absorption spectrum



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A. P. Alivisatos and Coworkers, Science 295, 2425 (2002)

Organic-Inorganic Hybrid Solar Cell

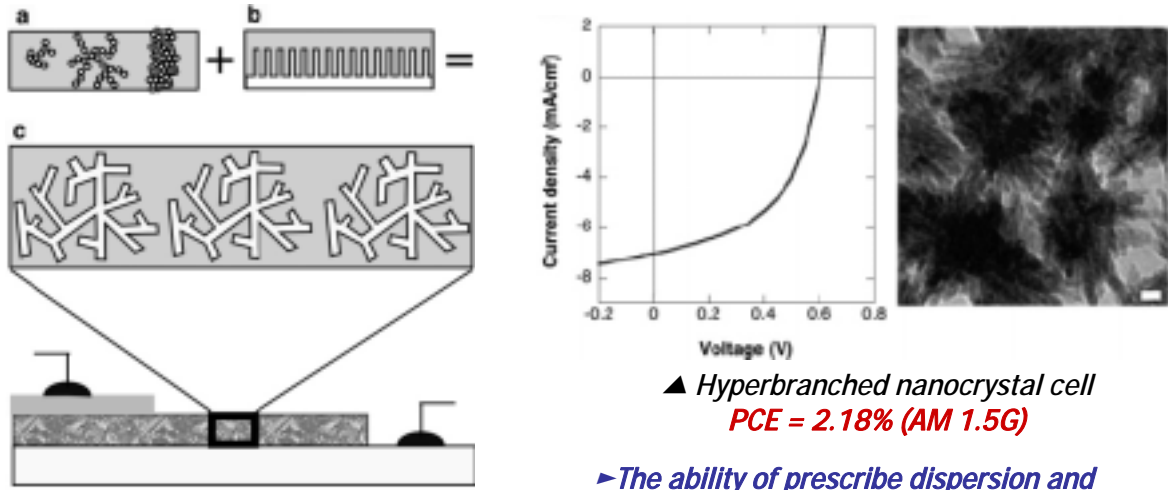


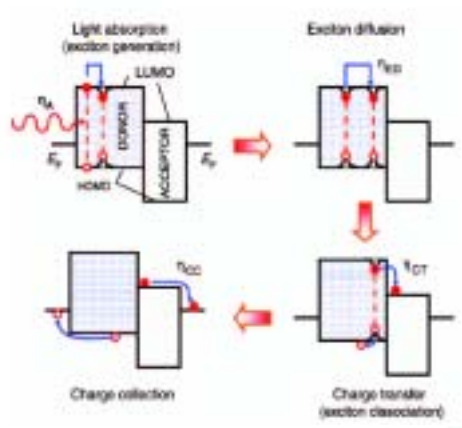
Figure 1. Hyperbranched nanocrystal solar cells. Hyperbranched nanocrystal solar cells combine the ease of fabrication of spin-cast hybrid devices (a) with the controlled morphology of templated approaches (b). Defects such as islands and aggregates detrimental to the performance of conventional spin-cast hybrid cells are eliminated in hyperbranched particle composites, where blend morphology is dictated entirely by the 3-D structure of the hyperbranched nanocrystal (c).

▲ **Hyperbranched nanocrystal cell**
PCE = 2.18% (AM 1.5G)

► The ability of prescribe dispersion and percolation characteristics of a composite device through choice of nanoparticle structure is perhaps the clearest advantage of hyperbranched nanocrystal solar cells over other hybrid architectures. Still, the efficiencies cited suggest that the CdSe nanocrystals used are far from optimal.

A. P. Alivisatos and Coworkers, Nano Lett., 7, 409 (2007)

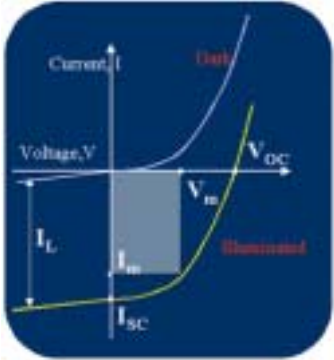
Mechanism of pn Heterojunction for organic PV cells



1. Exciton Generation
2. Exciton Diffusion
3. Charge Transport (Exciton Dissociation)
4. Charge Collection

$$\eta_{PCE} = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$$

A: Absorption; ED: Exciton Diffusion
 CT: Charge Transfer (Dissociation)
 CC: Charge Collection

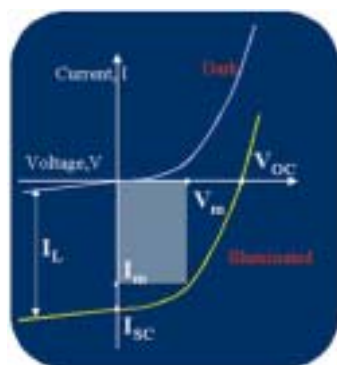


$$\eta(PCE)(\%) = \frac{P_{out}}{P_{in}} = \frac{V_{max} I_{max}}{P_{in}}$$

$$= FF \frac{V_{oc} I_{sc}}{P_{in}} \quad FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}$$

PCE: Power Conversion Efficiency
 FF: Fill Factor

How can we obtain high efficiency?



$$\eta(PCE)(\%) = \frac{P_{out}}{P_{in}} = \frac{V_{max} I_{max}}{P_{in}} = FF \frac{V_{oc} I_{sc}}{P_{in}} \quad \left(FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \right)$$

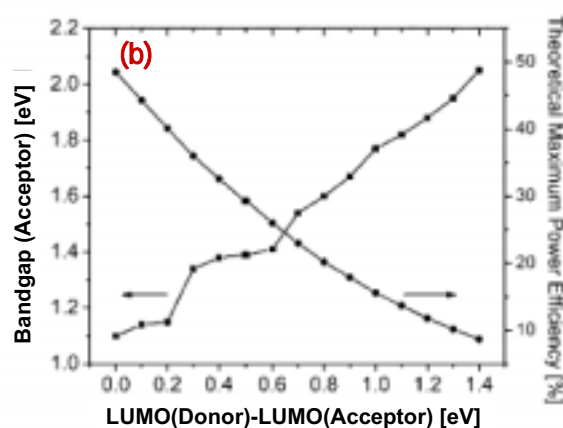
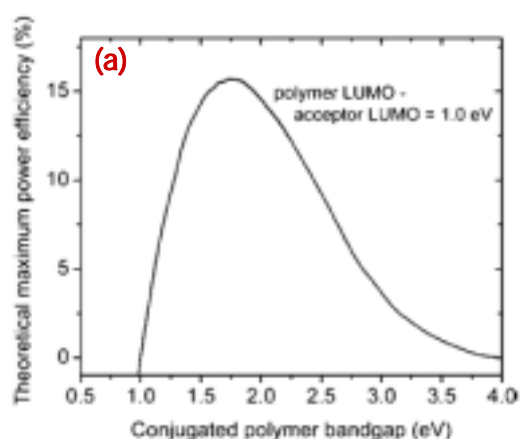
(i) to increase V_{oc}

- fabrication of structure with parallel cell connection (ex) polymer tandem solar cell
- materials with longer exciton diffusion length (ex) incorporation of nanometer size Ag particle

(ii) to increase I_{sc}

- synthesis of conjugate polymer with low bandgap
 - : Until now, conjugate polymer absorbs the light of visible region.
 - To absorb the light of near infrared region, the conjugate polymer with low bandgap is needed.
- materials that absorb solar radiation energy at $\lambda > 750\text{nm}$

Prospects for High-Efficiency Conjugated Polymer Photovoltaic Cells

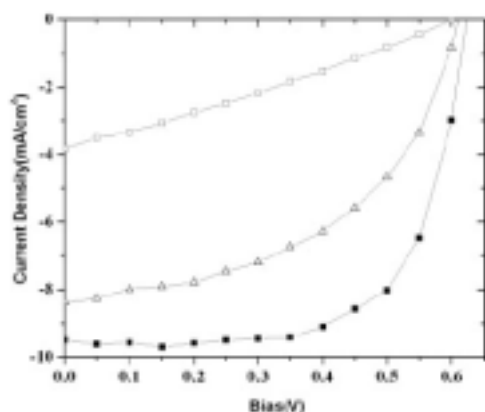


Michael D. McGehee, *Chem. Mater.*, 4533, 16, (2004)

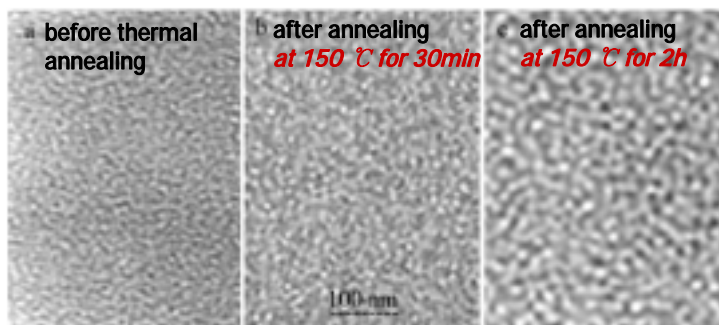
- Theoretical maximum power efficiency of a conjugated polymer-electron acceptor PV cell as a function of the polymer band gap when 1 eV of energy is lost during electron transfer.
- Optimal polymer band gap and theoretical maximum power efficiency as a function of the energy loss during electron transfer.

► Reaching 10-20% efficiency will come partially from better designed organic PV cell architectures, but it will also require the synthesis of new conjugated polymers with smaller band gaps, wider bandwidths, optimized energy levels, and higher carrier mobilities.

Thermal Annealing Effect of Polymer Solar Cells



P3HT:PCBM blend system



► Effects of post thermal annealing

(i) thermally induced morphology modification (improved nanoscale morphology)

: **more efficient charge generation!**

(ii) thermally induced crystallization (higher crystallinity & improved transport across the interface)

: **charge collection at the electrodes, reduced series resistance, higher FF (Fill Factor)**

► **High PCE (~5%) & Thermal stability**

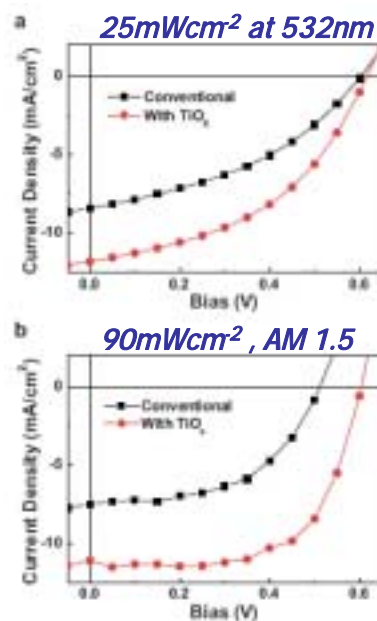
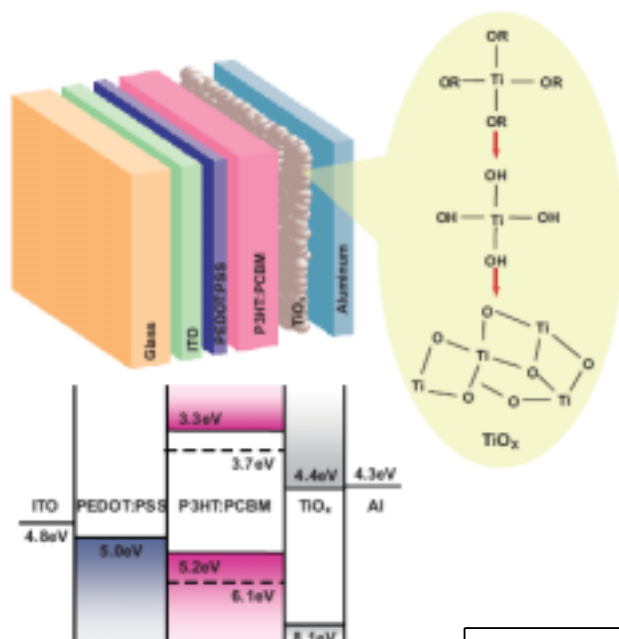
	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (Fill Factor)	η_e (PCE, %)
without thermal annealing	3.83	0.6	0.30	0.82
Post annealing at 70 °C for 30min	8.2	0.62	0.66	3.2
Post annealing at 150 °C for 30min	9.5	0.63	0.68	5

A. J. Heeger and K. Lee,
Adv. Funct. Mater., 15, 1617, (2005)



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Polymer Solar Cells using Titanium Oxide



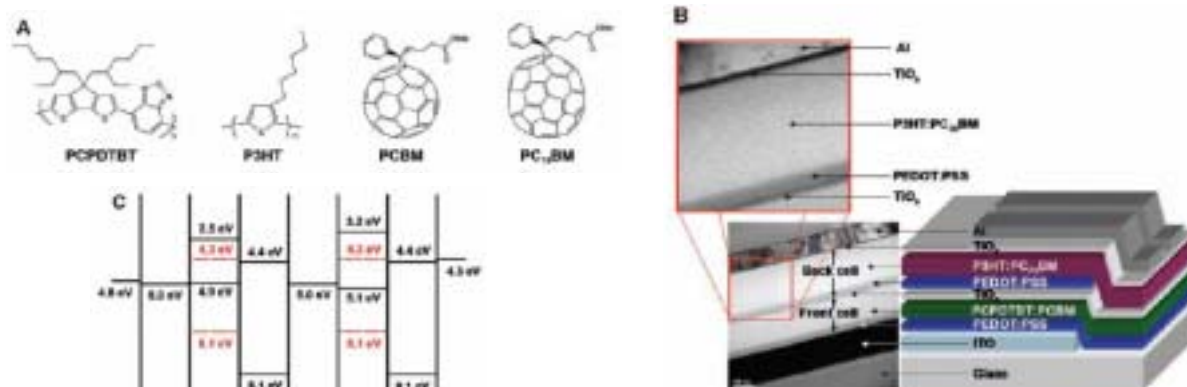
A. J. Heeger and K. Lee,
Adv. Mater., 18, 572, (2006)

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (Fill Factor)	η_e (PCE, %)
Without TiO _x	7.5	0.51	0.54	2.3
With TiO _x	11.1	0.61	0.66	5.0

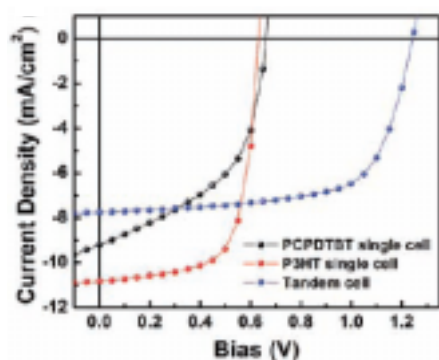


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Efficient Tandem Polymer Solar Cells



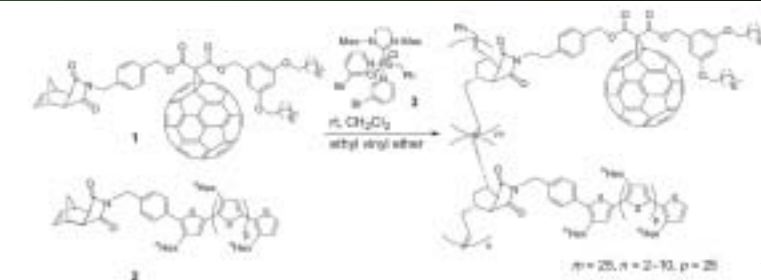
A. J. Heeger and K. Lee, *Science*, 317, 222, (2007)



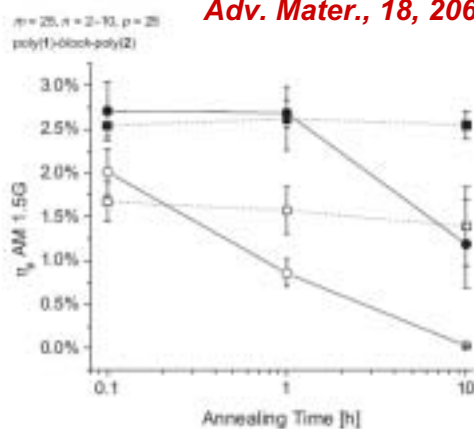
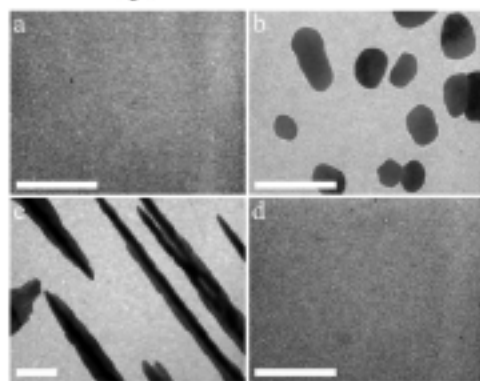
	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (Fill Factor)	η_e (PCE, %)
PCPDTBT:PCBM single cell	9.2	0.44	0.50	3.0
P3HT:PC ₇₀ BM single cell	10.8	0.63	0.69	4.7
Tandem cell	7.8	1.24	0.67	6.5

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Amphiphilic Diblock Copolymer Compatibilizers



Jean M. J. Fréchet, *Adv. Mater.*, 18, 206, (2006)



- a) 1:1 P3HT/PCBM blend before annealing
 b) after annealing (1h, 140°C)
 c) 1:1 P3HT/PCBM + 5wt% blockcopolymer after annealing
 d) 1:1 P3HT/PCBM + 17wt% blockcopolymer after annealing

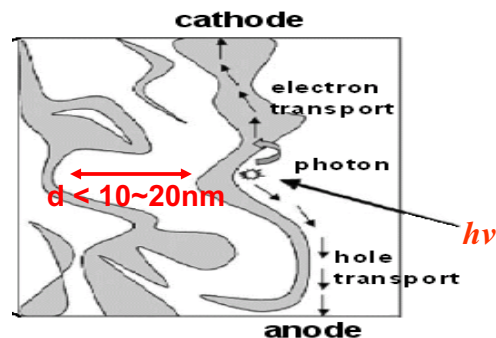
○, □ : before annealing ●, ■ : after annealing
 ○, ● : P3HT:PCBM
 □, ■ : P3HT:PCBM + 17wt% blockcopolymer

► adding small amounts of a diblock copolymer → lowering the interfacial energy between polymer and fullerene → change the morphology of blended thin film

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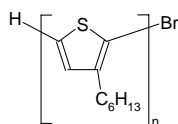
Motivation & System

How to control morphology of active layer?



P3HTs

Hydrophilic Modified P3HT



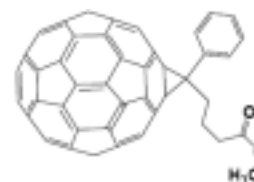
Reference

Hydrophobic Modified P3HT

Blend



PCBM



Miscibility?
Charge trap?
Ordering?

Treatment

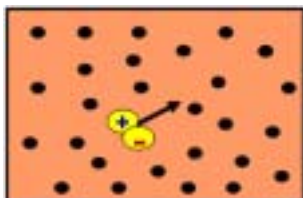
- Chemical traps for the direct trapping charges
- Quenching photogenerated excitons
- Chain packing defect by chain steric and electrostatic interaction
- Stability decrease through chemical reaction



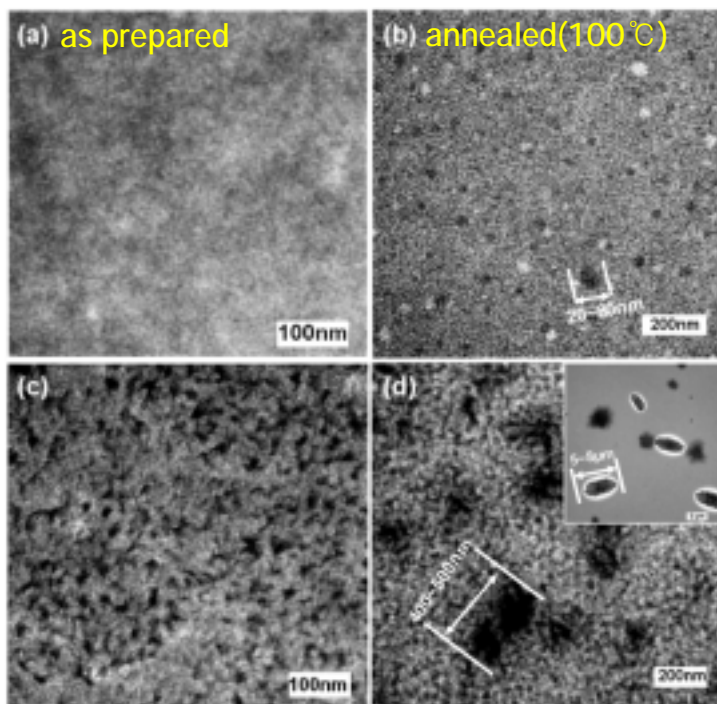
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Morphology

Hydrophobic Modified P3HT / PCBM



Hydrophilic Modified P3HT / PCBM



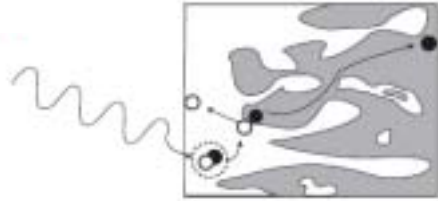
- PCBM domain size variation
- Exciton diffusion length matching
- Advantage of charge separation from exciton



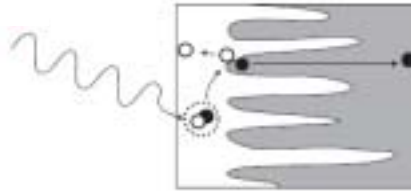
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Motivation & System

Conventional Bulk Heterojunction

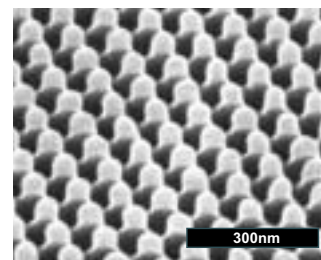
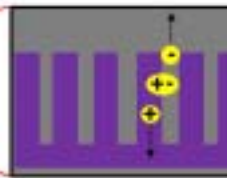
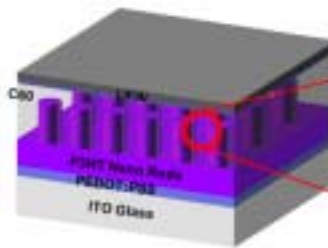


Ordered Bulk Heterojunction



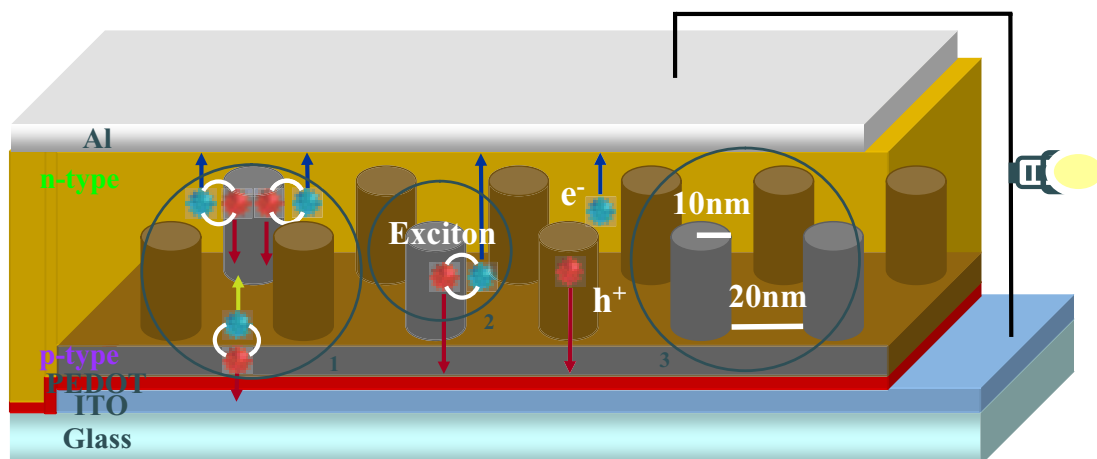
Ordered Bulk Heterojunction

- Exciton diffusion length
- Electron & hole pathway keeping
- Contact area \uparrow ($\sim \times 2.5$) \rightarrow optimum exciton separation
- Carrier transfer time \downarrow
- Back electron transfer \downarrow
- Exciton recombination loss $\downarrow \rightarrow I_{sc}$ increase



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Ideal Geometry of PN heterojunction PV device

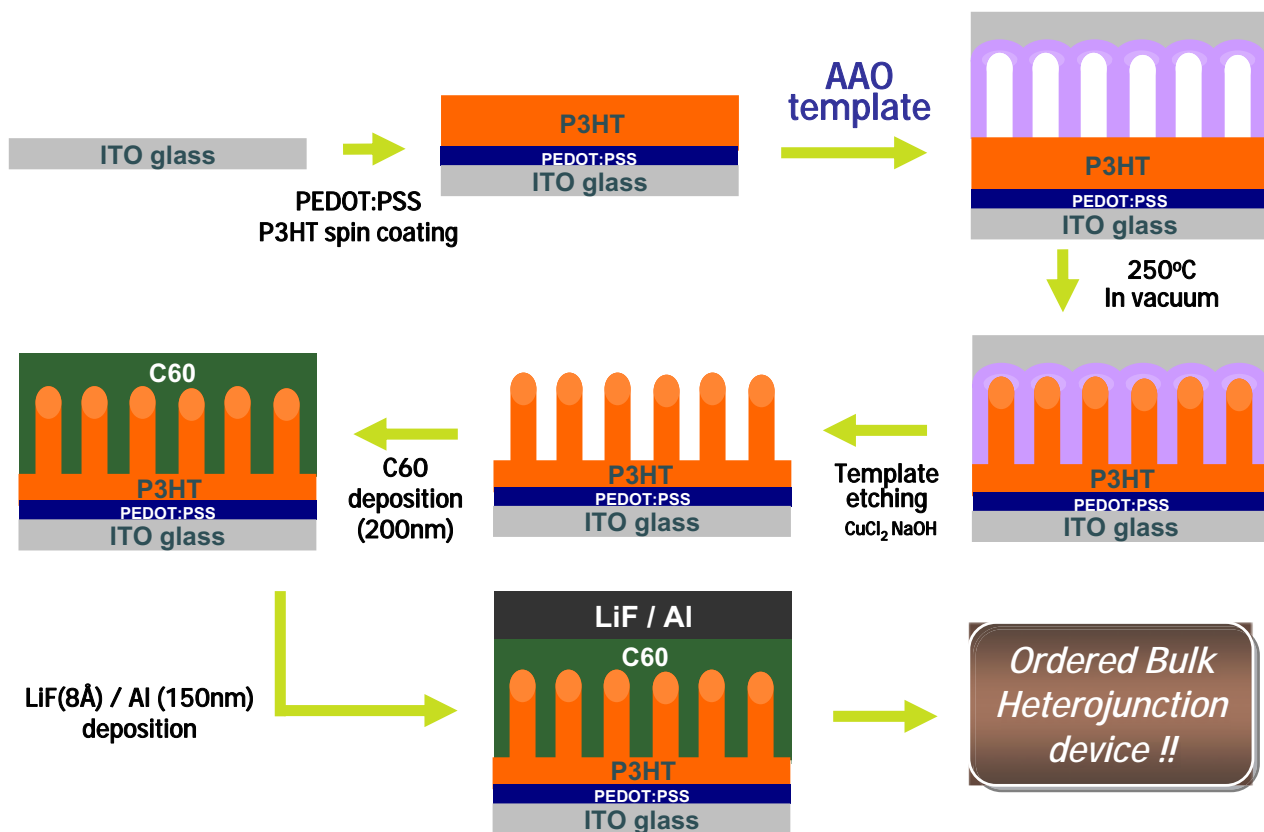


- Key Concepts:**
- 1) Increased p-n junction interfacial area
 - 2) Every exciton can arrive at the interface before disappearance by coupling (Maximum Dissociation)
 - 3) Good path way



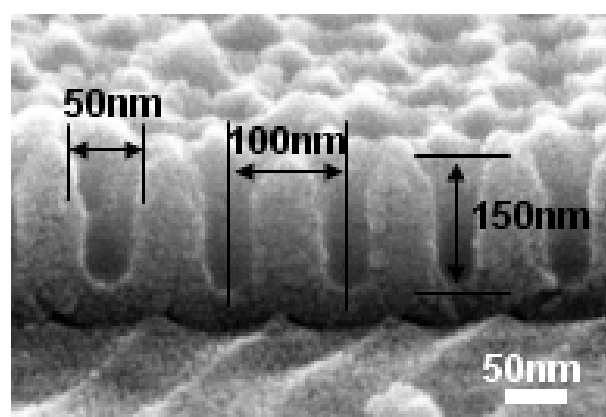
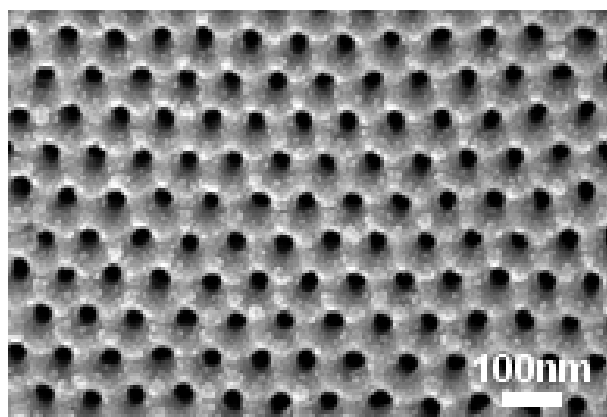
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Fabrication of P3HT Nano Rods and Ordered Bulk Heterojunction Solar Cell



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AAO Nanotemplates

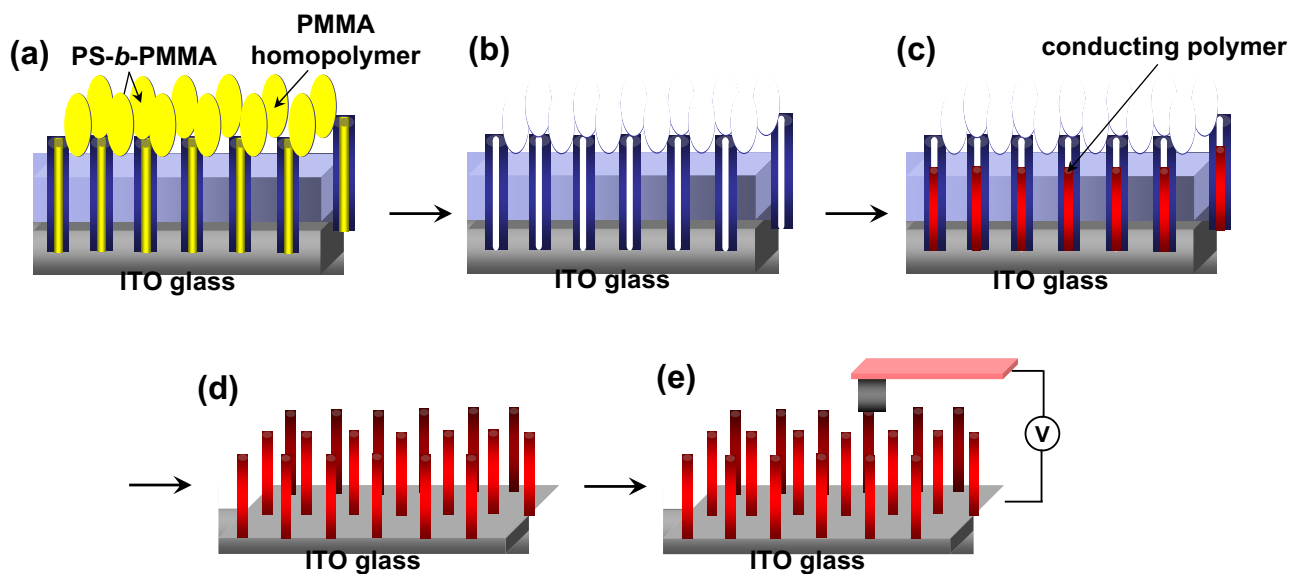


- Hole diameter ~ 50nm ← **P3HT**
- Inter-pore size ~ 100nm
- Hole depth ~ 150nm



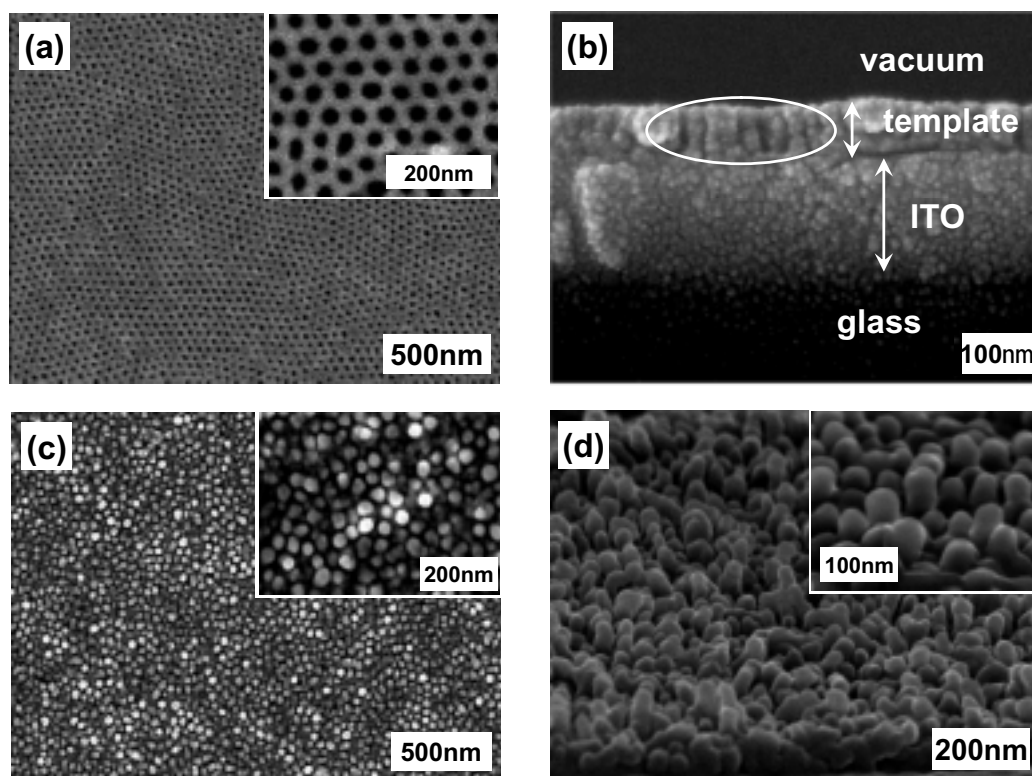
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Fabrication of Conducting Polymer Nanorod; Electropolymerization



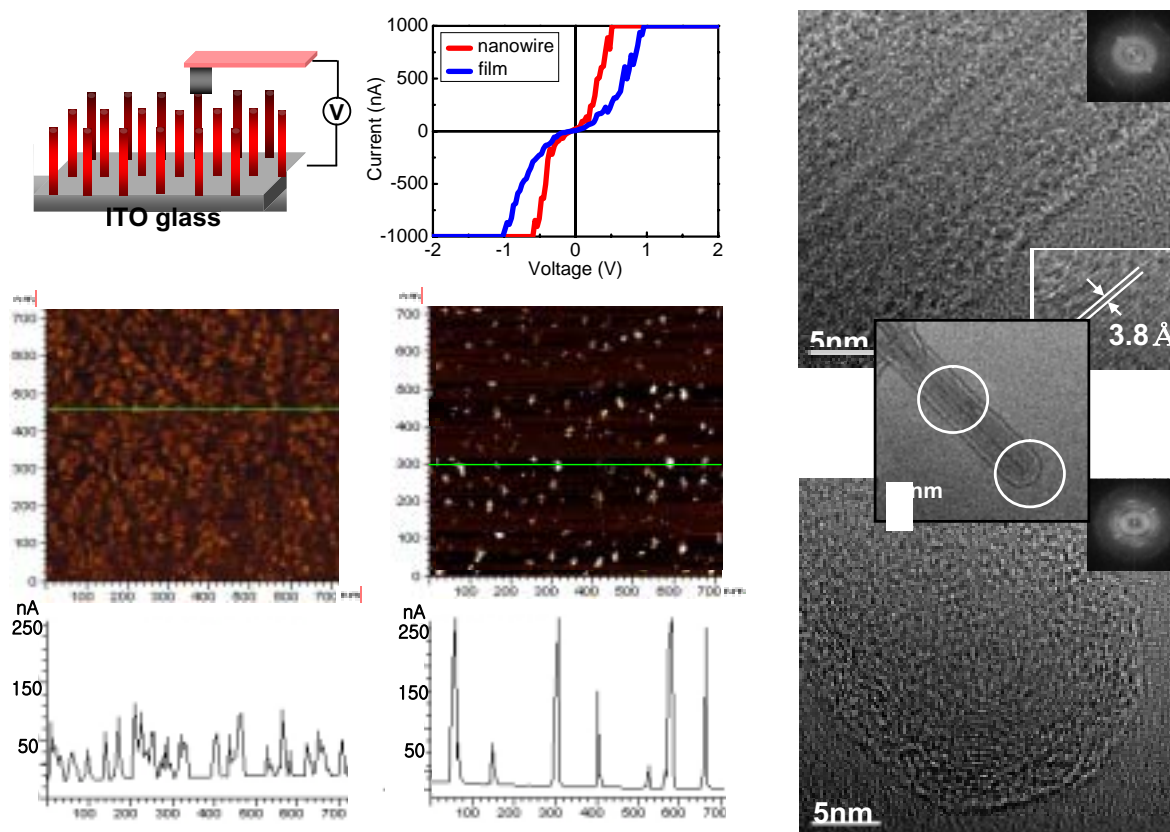
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Fabrication of Conducting Polymer Nanorod; Electropolymerization



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Fabrication of Conducting Polymer Nanorod; Electropolymerization

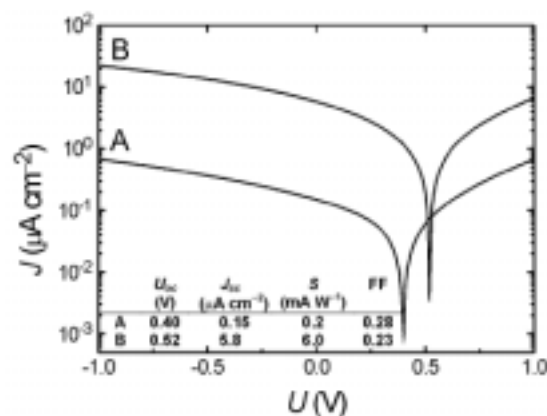


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Solar Cell using Semiconducting Diblock Copolymers



G. Hadziioannou and coworkers, *Polymer*, 42, 9097 (2001)



A : blend of D(donor) and A(acceptor)
B: PPV-b-P(S-stat-C₆₀MS) D-A block copolymer

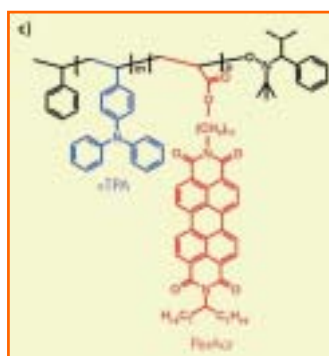
► The incorporation of C₆₀ moieties into one block of diblock copolymer was aimed at satisfying two requirements for efficient operation as a photovoltaic materials:

(i) creating an accessible D-A interface at which dissociation of excitons into separate charge carriers is promoted, thus reducing the probability of decay along other routes, of which luminescence is one;

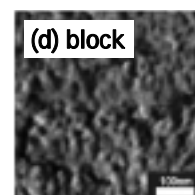
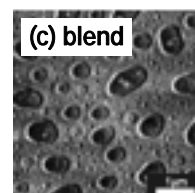
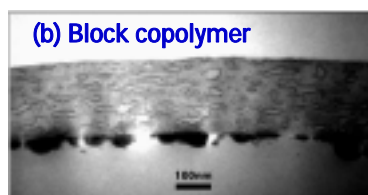
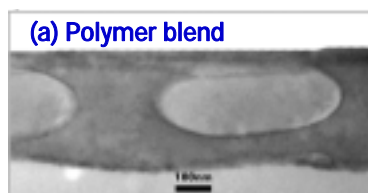
(ii) providing separate pathways for transport of holes (via PPV) and electrons (via C₆₀), thus reducing the recombination probability.

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Solar Cell using Block Copolymer

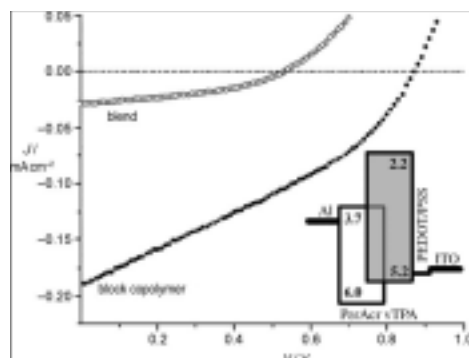


▲ Chemical structure of PvTPA-block-PPerAcr
vTPA=vinyltriphenylamine,
PerAcr=acrylate unit with perylene bisimide side group.



(a),(b)
Cross-sectional
image

(c),(d)
Surface
image



► Thickness ~ 250nm

	J_{sc} (mA/cm ²)	V_{oc} (V)	η (PCE, %)
Blend	0.028	0.525	0.007
Block copolymer	0.19	0.865	0.07

*M. Thelekkat and G. Krausch and coworker,
Angew. Chem. Int. Ed, 45, 3364 (2006)*



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Microphase-Separated Donor-Acceptor Diblock Copolymers



*M. Thelekkat and
coworkers, Adv.
Funct. Mater., 17,
1493 (2007)*

Block copolymer	M_n Block copolymer (g mol ⁻¹)	PDI Block copolymer	wt % PerAcr (¹ H NMR)	T_g [°C]	T_m [°C]
8 (a)	26.9	1.50	86	150	198
9a	34.6	1.76	72	131	183
9b	88.3	1.66	84	134	194
10	26.5	1.67	81	148	191

Block copolymer	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
8	0.23	670	0.32	0.065
9a	1.34	690	0.32	0.323
9b	0.24	530	0.32	0.052
10	1.21	530	0.31	0.262

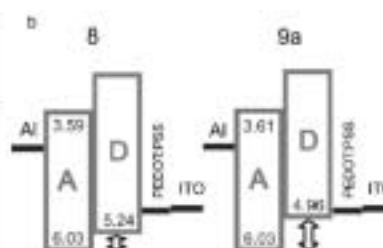
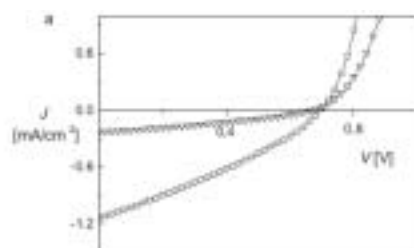


Figure 5. a) J-V characteristics of block copolymer 8 (●) and 9a (□). The measurements were carried out under white light illumination (AM 1.5 spectral conditions, 77 mW/cm²) in a N₂ atmosphere. b) Energy level diagram for both devices. In 9a the energetic driving force is higher because of a larger HOMO offset (represented by the arrow) compared with 8. The given acceptor LUMO level of 6.03 eV is determined from a low-molecular-weight perylene bisimide model compound. All energetic values are obtained from CV in solution.



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Solar Cells based on P3BT Nanowires

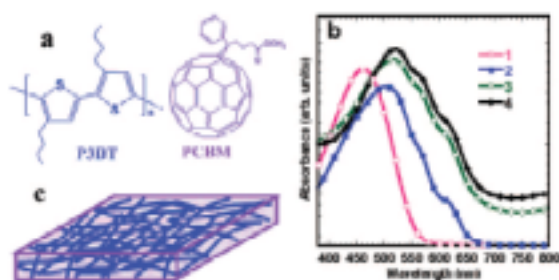


Figure 1. (a) Chemical structures of P3BT and C₆₁-PCBM. (b) UV-vis absorption spectra: (1) P3BT solution in ODCB; (2) P3BT-nw suspension in ODCB; (3) P3BT-C₆₁-PCBM blend on ITO/PEDOT substrate; and (4) P3BT-nw/C₆₁-PCBM nanocomposite on ITO/PEDOT substrate. (c) Schematic illustration of nanowire network of P3BT/PCBM composites.

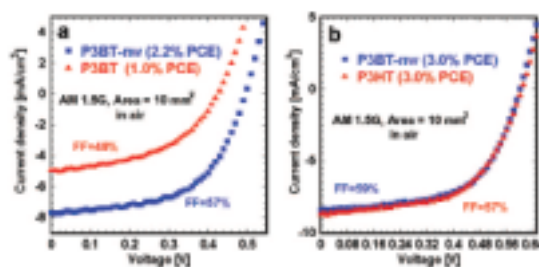


Figure 2. The current-voltage characteristics of solar cells with different active layers. (a) P3BT-nw/C₆₁-PCBM nanocomposite (1/1) (70 nm) (■) and P3BT-C₆₁-PCBM blend (1:1) (80 nm) (▲). (b) P3BT-nw/C₇₁-PCBM composite (1/0.75) (90 nm) (■), P3HT/C₇₁-PCBM (1:1) blend (120 nm) (▲). The films in panel a were dried in a vacuum oven at 60 °C overnight and films in panel b were annealed in a glovebox at 110 °C for 10 min.

S. Jeneke, JACS, 130, 5424 (2008)

► **highly efficient polymer/fullerene (both C₆₁-PCBM and C₇₁-PCBM were employed) solar cells in which a 3-D network of preassembled polymer-semiconductor nanowires serves as the donor component in a sea of fullerene acceptors.**

- an electrically bicontinuous nanoscale morphology is realized without going through the difficult path of blend phase-separation phenomena.
- poly(3-butylthiophene) nanowires (P3BT-nw) as the donor and C₇₁-PCBM as the acceptor
 - : 3.0% PCE (at 100 mW/cm², AM1.5, 10 mm² device area, in air)
 - P3HT/C₇₁-PCBM blend photovoltaic : 3.0% PCE.

► **P3BT can exhibit photovoltaic properties that are comparable to the much studied P3HT !!**



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Conclusion

- We fabricated hexagonal array of P3HT Nano-Rods oriented perpendicularly to the ITO glass by using AAO template. Crystalline orientation of P3HT in nanorods enhanced conductivity as much as a factor of 10 compared with the continuous P3HT film. With the increasing of interface area between donor and acceptor, PL intensity was dramatically decreased.
- With the increase of interfacial area and the P3HT molecular orientation, higher OPV efficiency was obtained compared with P3HT film. (~1.12%, X 6.6)
- Well-aligned Polypyrrole(Ppy) nanorods and CdSe nanorods were obtained using block copolymer templates. And Ppy nanorods has higher conductivity compared to continuous Ppy film due to chain orientation of nanorods grown inside nanohole.
- We controlled the domain size from miscibility control between PCBM and modified P3HT. The surface energy matching between PCBM and hydrophobic treat P3HT was most favorable.
- **Plenty of Room for enhanced efficiency by chemical modification as well as structure (Chemical Engineering combined with Synthesis and Physics)**



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Acknowledgment

- National Creative Research Initiative Center for Block Copolymer Self-Assembly
Supported by KOSEF

-J. W. Yu (KIST)

-K. W. Cho (POSTECH)

Jeong In Lee
Phillip Antony
SungChul Kwon



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