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Supra-hierarchical nano-structured organic thin film solar cell

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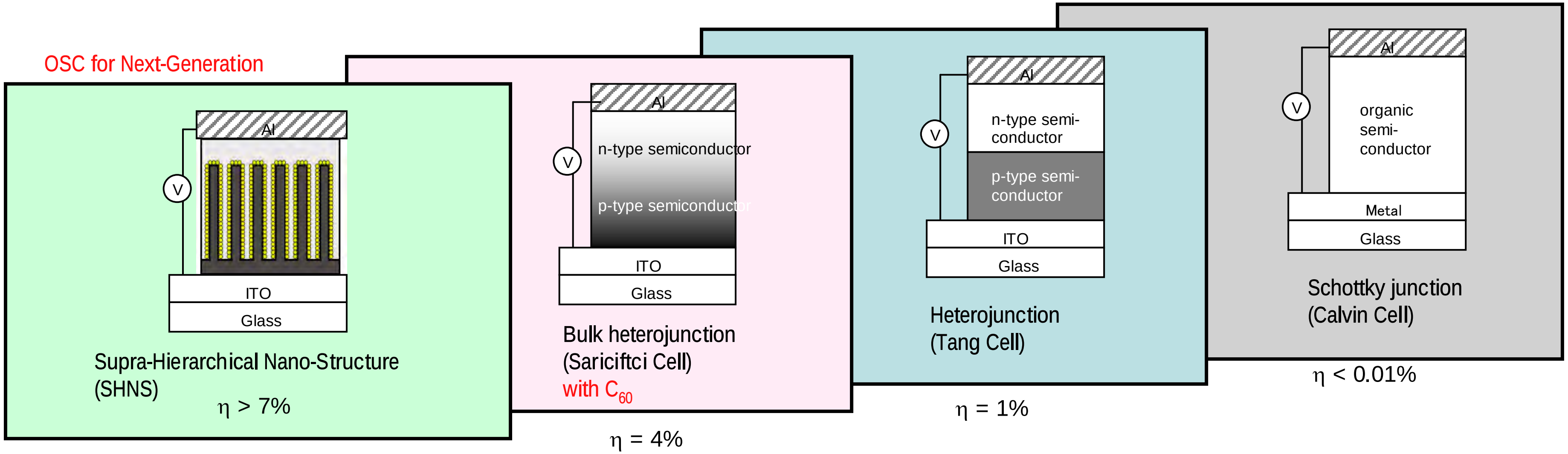
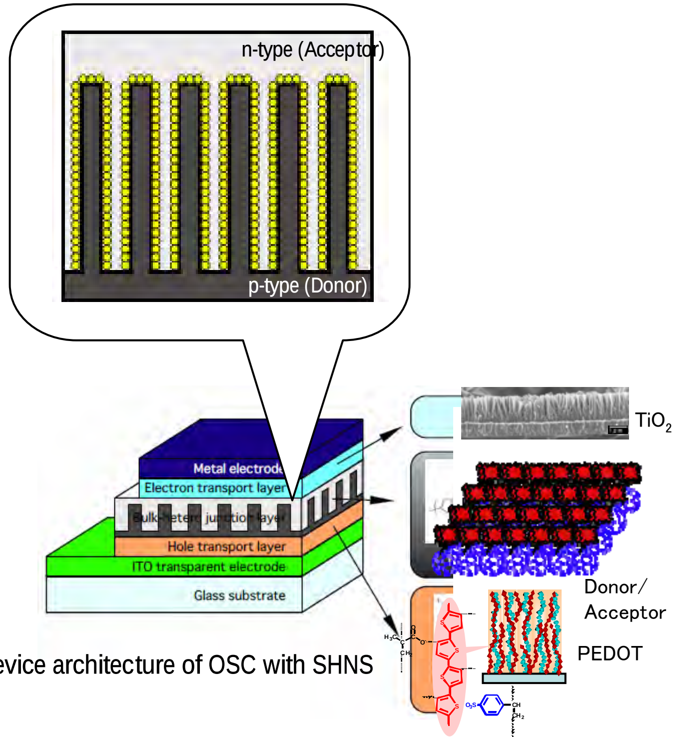
Contents

- ☐ Insertion of TiO_2 ETL in polymer solar cell of P3HT:PCBM
- ☐ Preparation of PEDOT:PSS polymer brush as HTL in polymer solar cell
- ☐ Concept of Supra-hierarchical nano-structured cell (Hybrid solar cell)

Biography of Organic Solar Cell & Novel Architecture of OSC with Supra-Hierarchical Nano-Structure



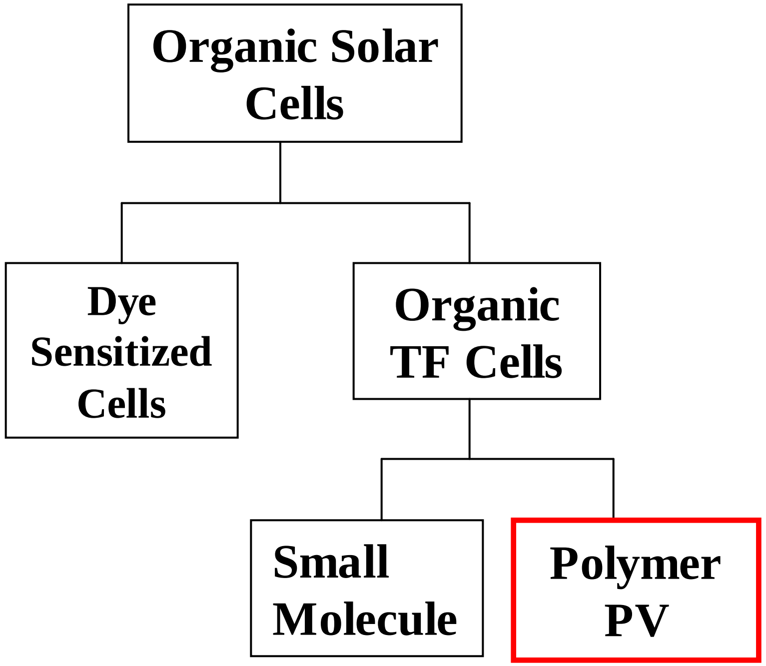


Device architecture of OSC with SHNS

2006 supra-hierarchical nano-structured cell (*Yoshikawa*)
2004 tandem heterojunction photovoltaic cell (Forrest, *Uchida*)
2000 bulk MDMOPPV/PCBM heterojunction PV cell (Brabec)
1996 C_{60}-linked molecular type PV cell (*Imahori*)
1995 bulk MEHPPV/PCBM heterojunction PV cell (Heeger)
1995 bulk polymer/polymer heterojunction PV cell (Friend)
1994 bulk polymer / C_{60} heterojunction PV cell（Heeger）
1993 polymer/ C_{60} heterojunction PV cell (Sariciftci)
1991 dye-sensitized TiO_2 PV cell (Graetzel)
1991 bulk dye/dye heterojunction PV cell (*Hiramoto*)
1990 tandem PV cell (*Hiramoto*)
1986 heterojunction PV cell (Tang)
1958 photo-induced current with MgPor (Calvin)

Topics are focused to improvements in device structures.

Introduction



Current status of polymer solar cell

- **Recently high efficiencies over 5% are reported.**
- **Poly(3-hexylthiophene)/PCBM is commoly used as a high carrier mobility system.**
- Bulk heterojunction is important for highly efficient cell-structure.

Advantages of polymer PV

- **Fabrication under ambient atmosphere**
- **Potential low-cost manufacturing**

Problems of Organic PV

- **Low efficiency**
- **Low durability**

Organic Semi-conductors

Comparison, organic and inorganic meterials

	mobility *[cm²/Vs]*	*anisotropy*	*Cohesion Force*
Inorganic	~1000	few times	Chemical bonding
Organic	~10	~100 times	van der Waals

organic materials:

origin of electric conduction ⇒ planer π -conjugated molecule

Fundamental Limitations to Organic Solar Cells

The exciton and carrier diffusion bottleneck

Since L_D is short & μ is little, there exists a trade off in thickness.

Problems

Maximum: exiciton collection & Minimum series resistance ⇒ thin film

Maximum: absorption ⇒ thick film

How to solve these problems?

- **Using a bulk heterojunction**
- **Using material with long range order**
- **Using thin HTL and ETL with EBN and HBN**
- **Using tandem cells (capture more light in thin layer**
- **Using 1D nanostructured array for carrier path**

  （Supra-hierarchical nano-structured cell)

- Insertion of electron transport layer (ETL) in polymer solar cell
  - P3HT: PCBM with **TiO_2 layer**

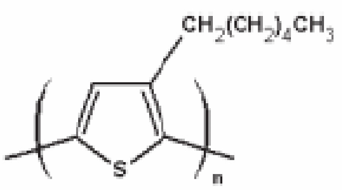
Organic Thin Film solar Cell

Enhanced efficiency and stability in P3HT:PCBM bulk heterojunction solar cell by using TiO_2 as electron transport layer

Necessity of hole blocking layer in polymer cell

TCO	→ ITO glass
HTL	→ PEDOT:PSS
LAL	→ P3HT:PCBM
HTL	→ Nothing (LiF) **←TiOx層**
anode	→ Al

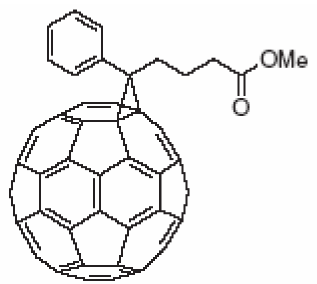
To achieve highly efficient charge transfer and charge collection



P3HT

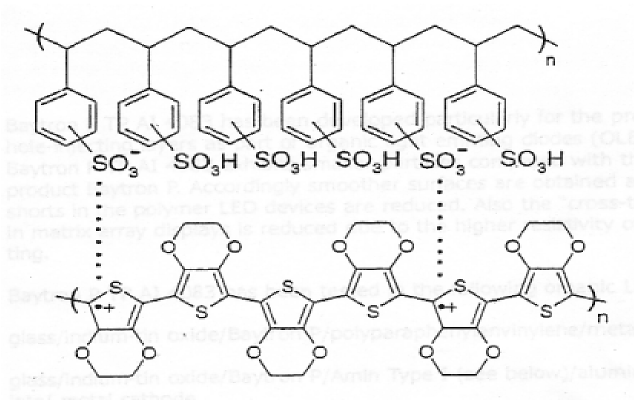
Poly (3-hexyl thiophene)

[P3HT]



PCBM

[6,6] -phenyl C60-butyric acid methyl ester [PCBM]



Poly (3,4-ethylenedioxythiophene) - poly (styrensulfonate) [PEDOT:PSS]

Necessity of HBL (hole blocking layer)

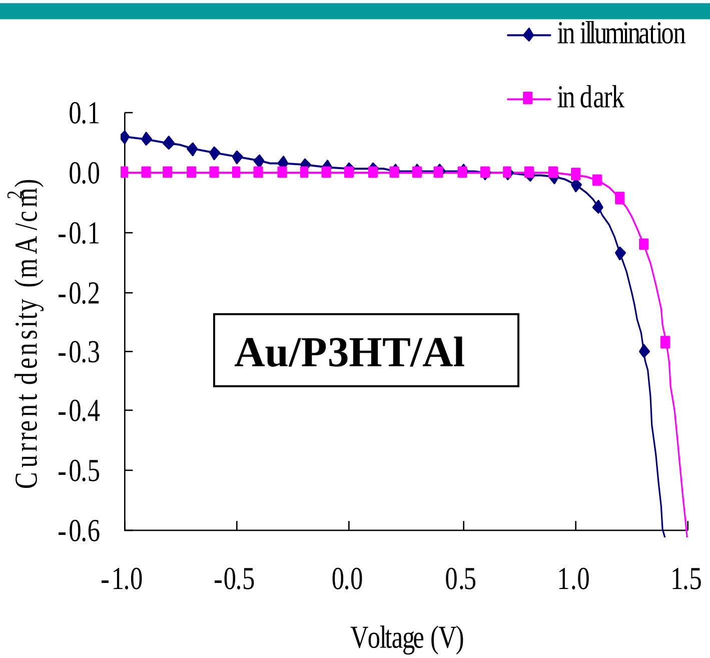


Fig.3 I-V curve of Au/P3HT/Al in dark and under illumination.

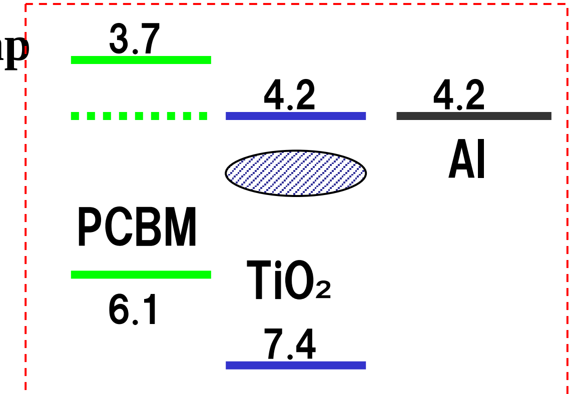
In dark, P3HT/Al interface forms a Schottky barrier to prevent a back electron transfer and shows a favorable rectification.

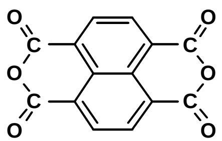
Under illumination, I-V curve shows a less rectification. → **Increase in a back electron transfer**

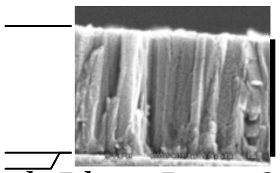
Necessary to introduce a new barrier

Conditions for HBL

- **n-type semiconductor**
- **LUMO is between Al and PCBM**
- **A wide band gap**







NTCDA as HBL
Ag/C_{60}/CuPc/ITO
2 μm

Hiramoto, Appl. Phys. Lett., **86**, 063509 (2005).

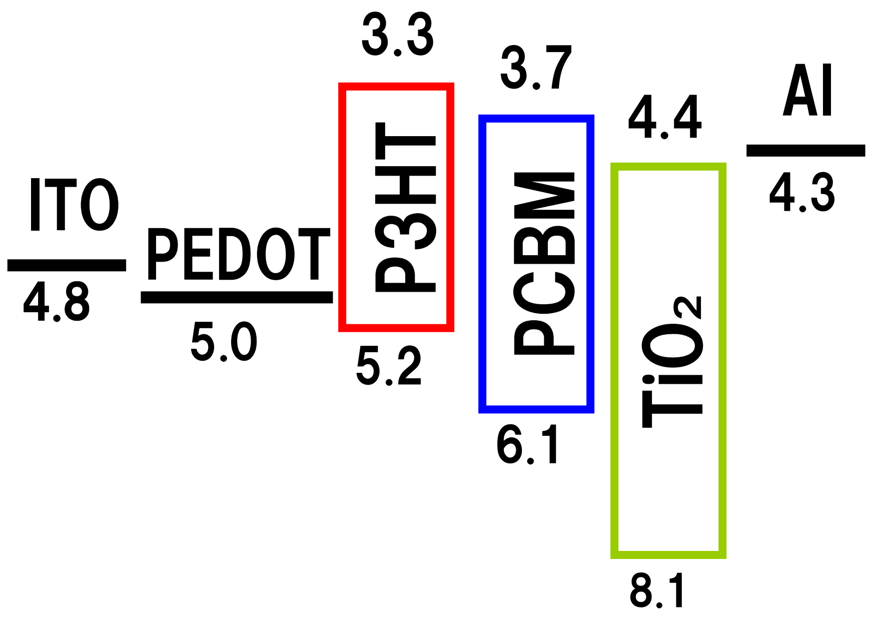
Energy diagram of TiO_2

Hal et al. reported

P.V.A. Hal et. al., *J. Adv. Mater. 2003, 15, No.2*

Ti-alkoxide $\xrightarrow{\text{room temperature over night}}$ • TiO_2 (77～91%)

TiO_2 prepared by this method has an amorphous structure



UV-Vis and cyclic voltammetry suggest that band gap is 3.7 eV、

HOMO is 8.1 eV、

LUMO is 4.4 eV

Fig.8 Flat band potentials of ITO/PEDOT/P3HT:PCBM/Al.

Use of TiOx layer as optical spacer, K. Lee, et. al., Adv. Mater. 2006, 18, 572

Effects of TiO_2 film thickness on photovoltaic properties

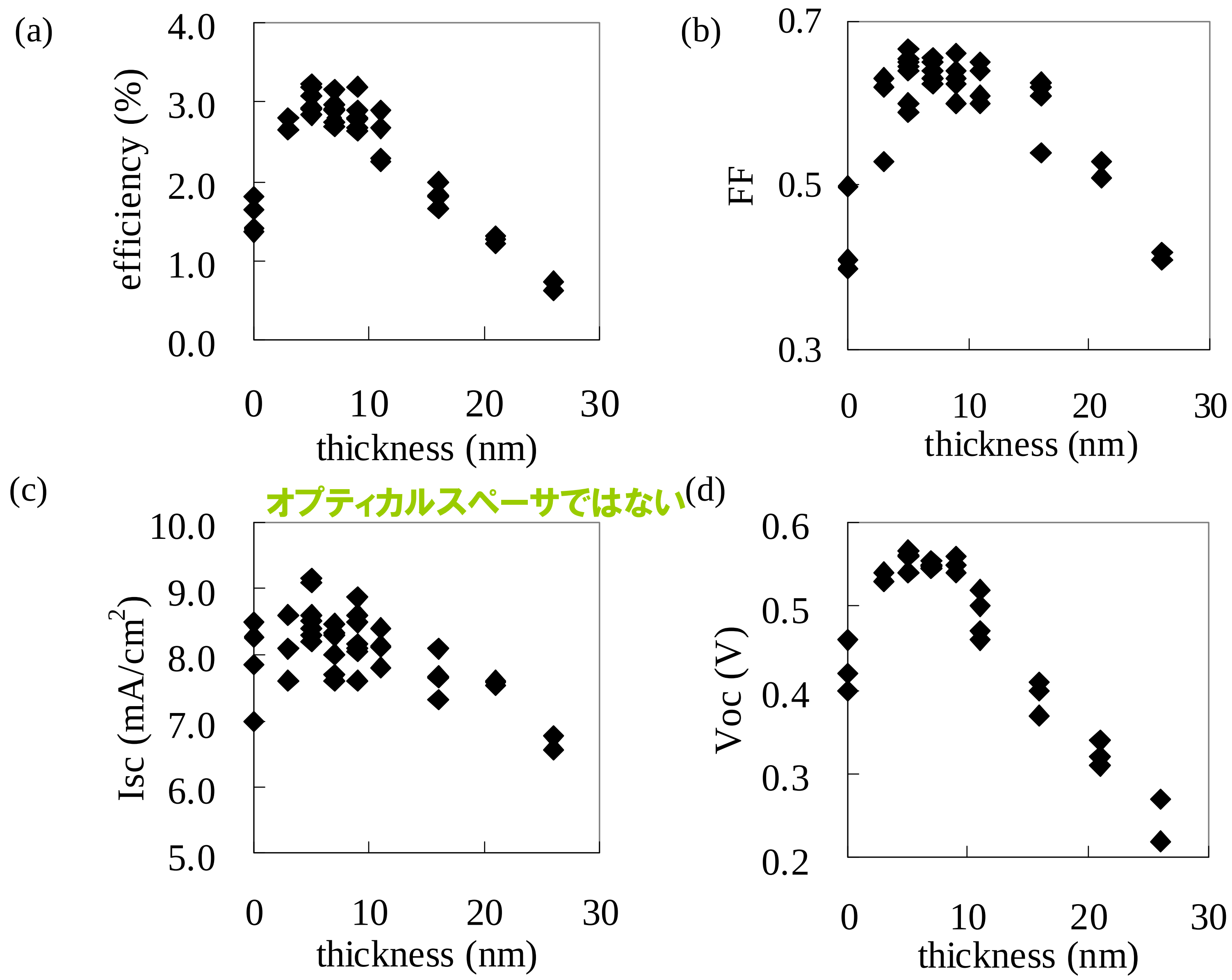
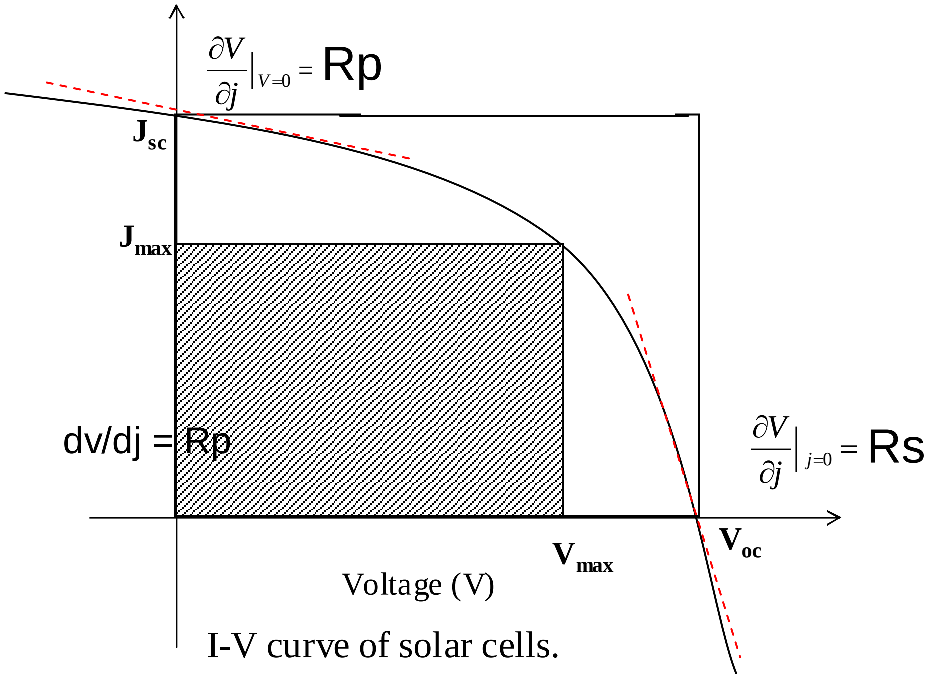


Fig.10 Effect of TiO_2 on Efficiency (a), FF (b), Voc (c), Isc (d).

Evaluation method of organic solar cell

Simulated sun light of A.M. 1.5G 100mW/cm² was illuminated onto the cell.

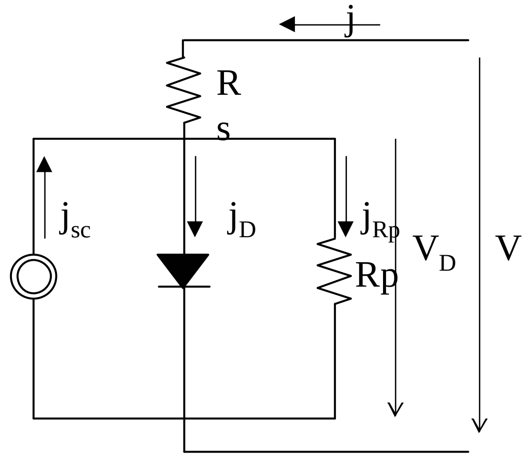


I-V curve of solar cells.

$$FF = \frac{P_{max}}{V_{oc} \cdot J_{sc}} = \frac{V_{max} \cdot J_{max}}{V_{oc} \cdot J_{sc}}$$

$$\eta = \frac{P_{max}}{P_{light}} \times 100 = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{light}} \times 100$$

Series resistance（Rs） and parallel resistance (Rp)



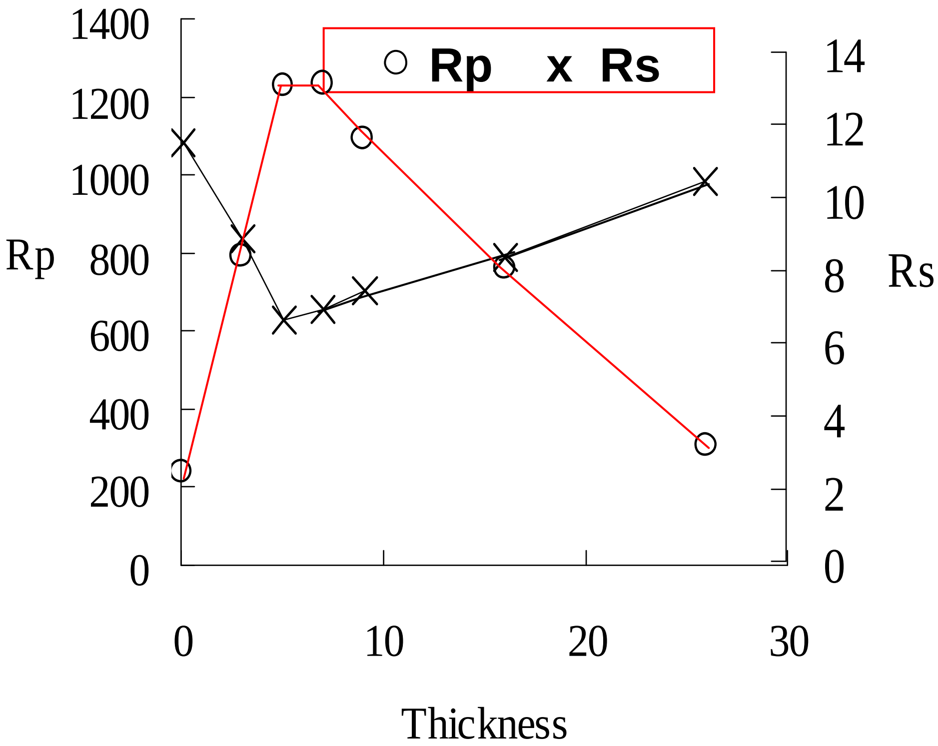
Equivalent circuit of solar cells.

Reduce in an internal resistance
→ decrease in Rs
→ increase in Isc

Improve of carrier selectivity
→ increase in Rp
→ increase in Voc

Rp inclease and Rs decrease by TiOx insertion

① Series resistance（Rs）and parallel resistance（Rp）

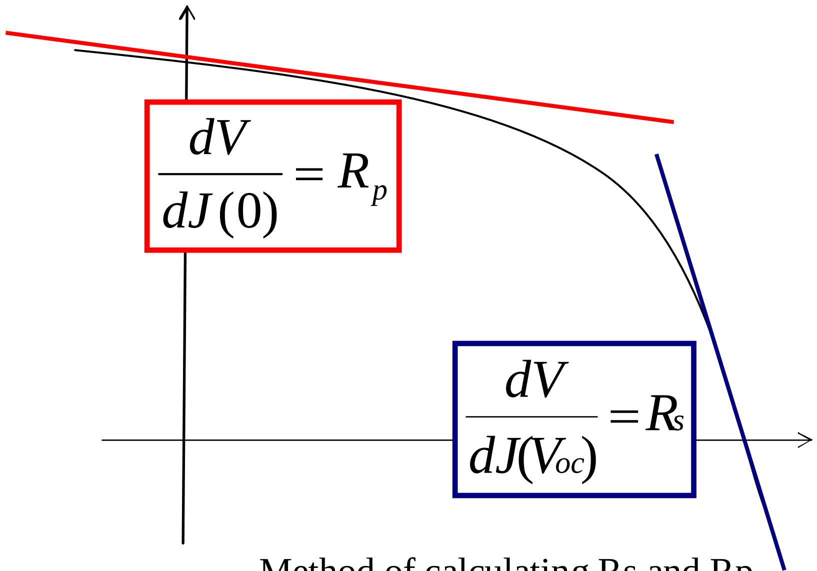


Rp and Rs of devices containing TiO_2 layer with several thicknesses.

Reduce in an internal resistance
→ decrease in Rs

Improve of carrier selectivity

→ increase in Rp



Method of calculating Rs and Rp.

Insertion of TiO_2 layer induced a marked increase in Rp

→ Improve of carrier selectivity

Rectification ratio

② **Change in rectification ratio (RR)**

$$(RR) = -\frac{I_{(-2V)}}{I_{(2V)}}$$

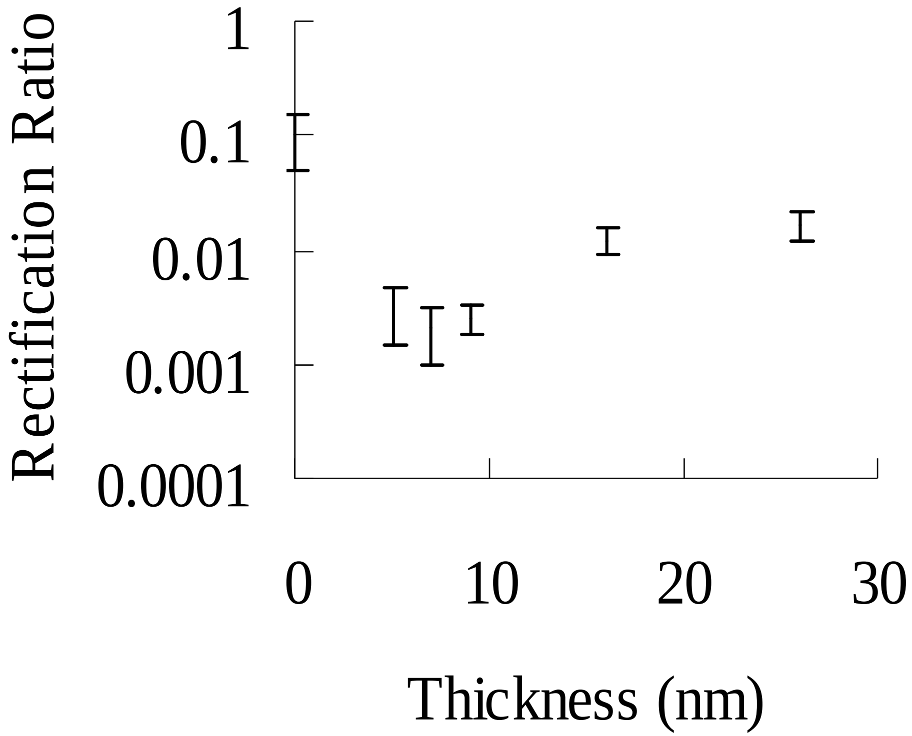


Fig.13 The ratio of the current density of devices with several thickness TiO_2 at ＋2V an －2V in dark.

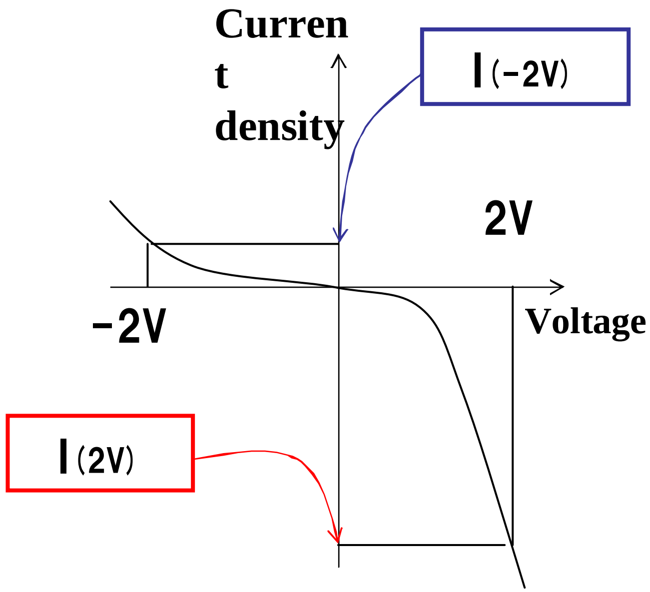


Fig.14 Method of calculating RR.

Improvement of rectification by insertion of TiO_2 layer → TiO_2 layer blocks hole carriers.

Conclusions

- Improved cell structure with TiO_2 layer on active layer (P3HT:PCBM) is quite promising.
- TiO_2 layer acts as a hole blocking layer.
- Optimal 4% conversion efficiency was obtained with very high fill factor under ambient atmospheric condition without sealing.
- Isc of the device with TiO_2 decreased only 6% after 100 hour illumination, showing high durability under ambient atmospheric condition.

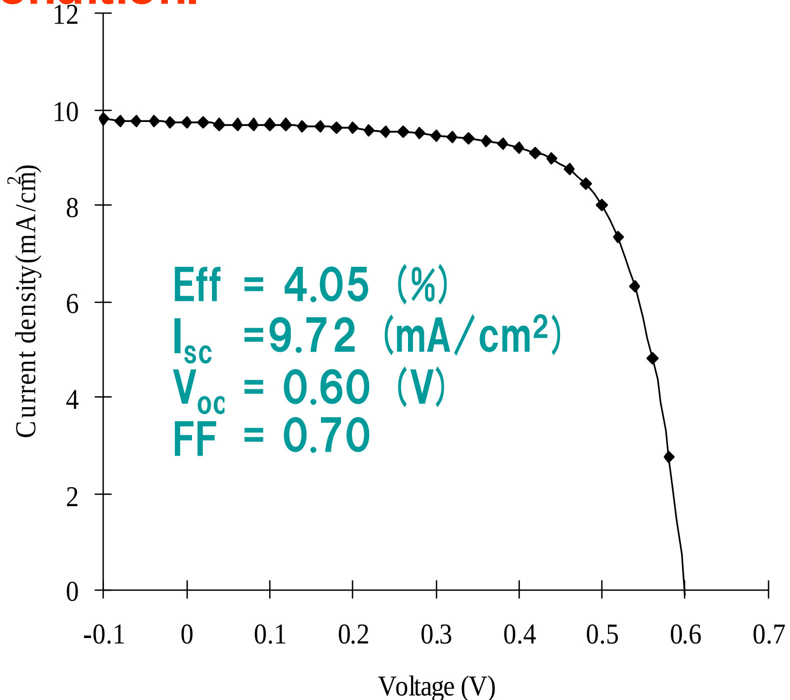


Fig.22 I-V curve of the best cell.

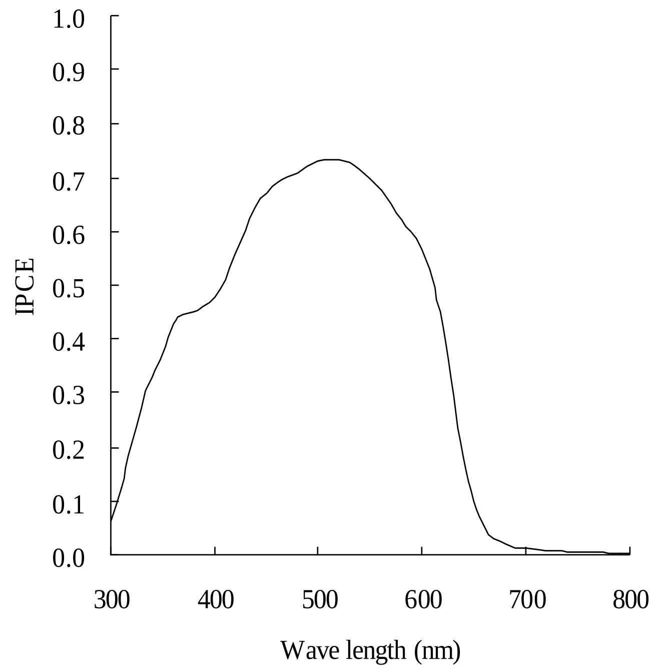


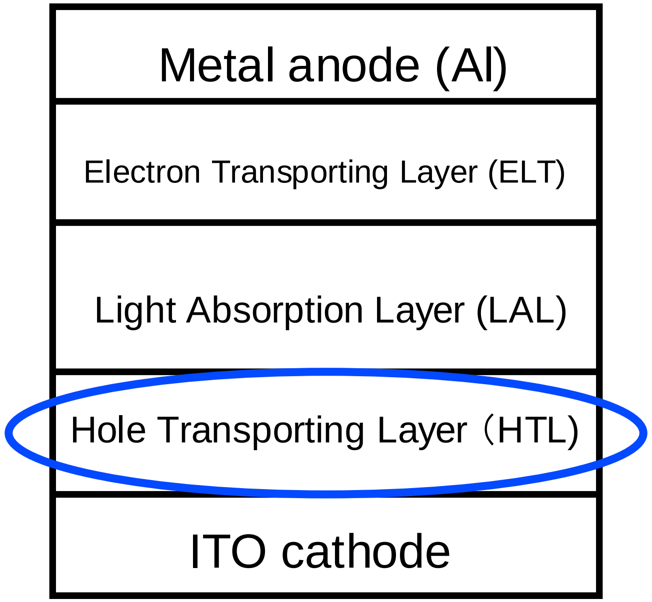
Fig.23 IPCE spectrum of the best cell.

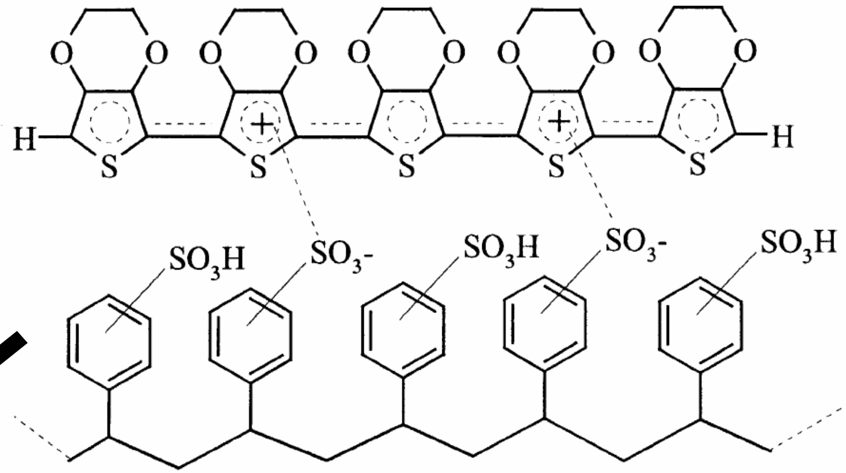
- ☐ Preparation of hole transport layer (HTL) using PEDOT:PSS polymer brash

Organic Thin Film solar Cell

Rolls of Hole Transporting Layer (HTL)

Organic Thin-Film Solar Cells





PEDOT:PSS
Poly(3,4-ethylenedioxythiophene)-poly(styrensulfonate）

PEDOT/PSS

- ●PEDOT:PSS films help to planarize the ITO surface
- ●PEDOT:PSS films appear to make the ITO surface more uniformly electroactive
- ●PEDOT:PSS layer reduces the electrode surface polarity, making it more compatible with nonpolar components of OPVs
- ●PEDOT:PSS layer appears to increase the effective work function of the resulting substrate

highly rectification (electron blocking) ability (large carrier mobility and/or conductivity), transparency, low resistance at the interface, and so on.

The HTL plays a key role in the OPVs.

PEDOT/PSS: What is the problem?

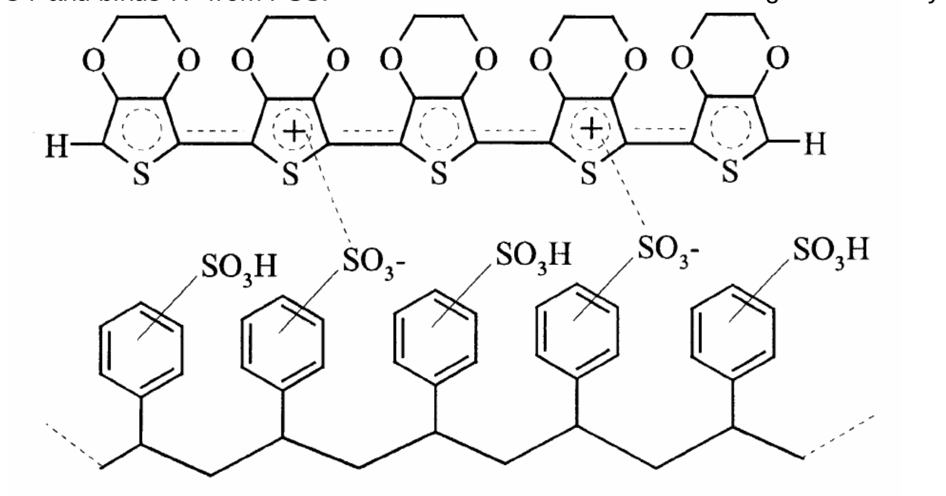
- Low solubility→ Hard to be processed→ Unsuitable for thin-film-making
- Dispersed in water → Water is unsuitable for electronic manufacture such as coating
- Impossible to be coated on the substrate such as glass or electrode without the binder→ Lack of adhesion to the substrate
- High acidity, corrosive, absorbent material→ ITO is eroded
- No durability against water, other solvents, and scratching

We need novel materials for **HTL**s.

- **Neutralized and dispersed in organic solvents →No corrosive for ITO and no desiccant**
- **Directly polymerized from the glass or electrode without the binder**
- **High density without pin-hole →Decrease the resistance at the interface and enhance the physical stability of the film**

Doping of PSS cuts the π conjugation of PEDOT and binds H^+ from PSS.

Isolated π electron migrates along the PEDOT chain shows high conductivity.



PEDOT:PSS

Poly(3,4-ethylenedioxythiophene)-poly(styrensulfonate)

Polymer brush

Control of ATR polymerization of SSNa, SSEt on ITO

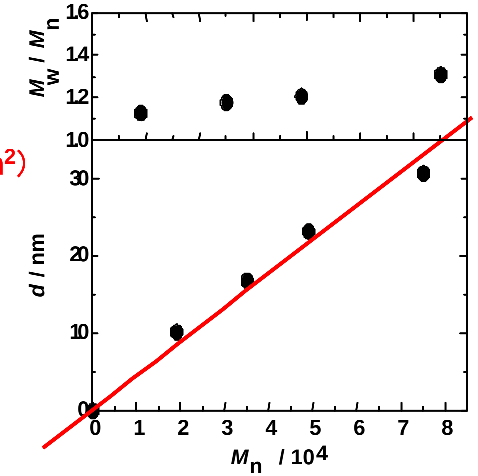
Highly dense polymer brushes were obtained.

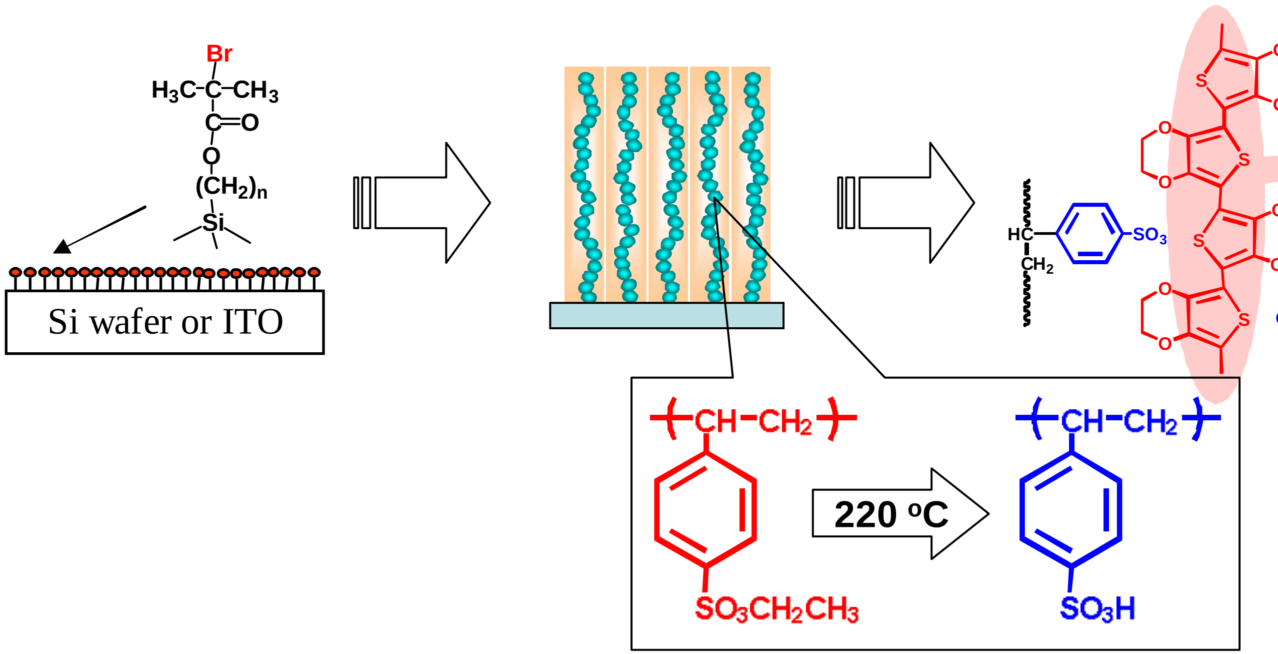
PSSNabrush：surface density 37%, PSSEt brush：38%（grafted density：0.26 chains/nm^2）

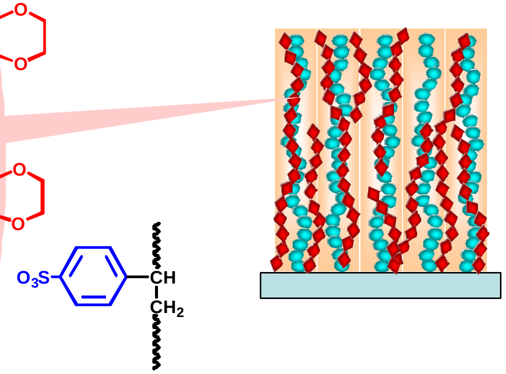
Highly expanded and oriented polymer brush in water and/or CH_3CN

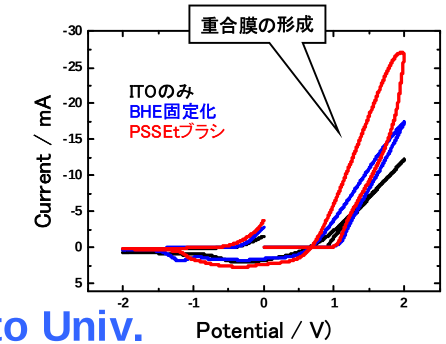
In situ polymerization of EDOT

［PSS brush：chemical oxidation, PSSEt brush：electrochemical polymerization］



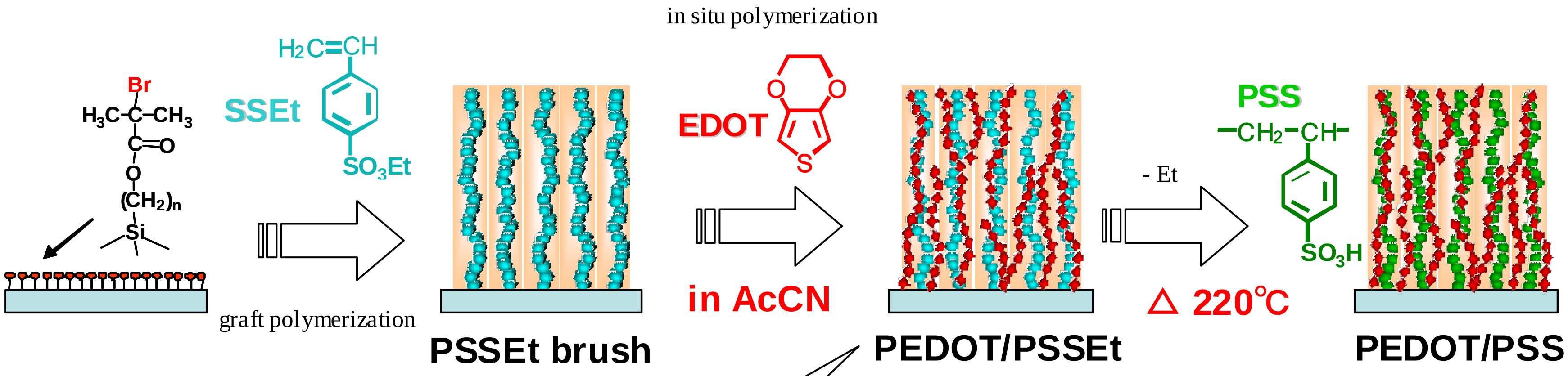




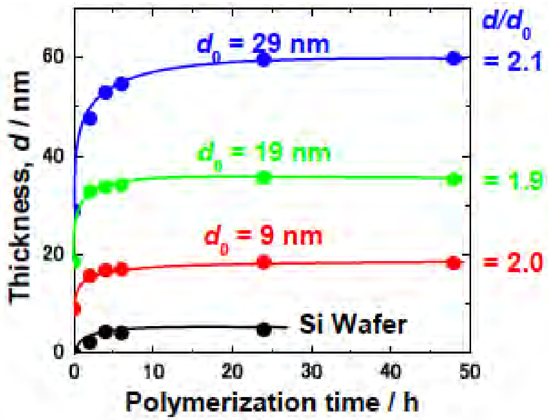


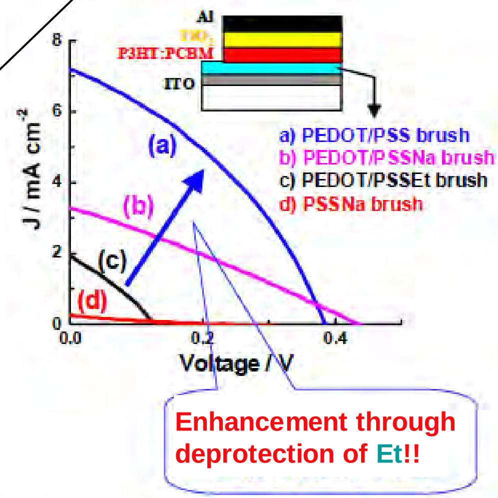
Prof. Y. Tsujii, *et al*, Institute for Chemistry, Kyoto Univ.

Polymer brush

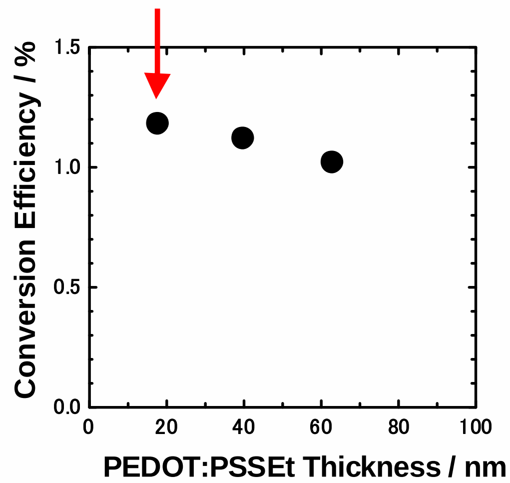


Highly ratio of PEDOT component





18nm (very thin!)

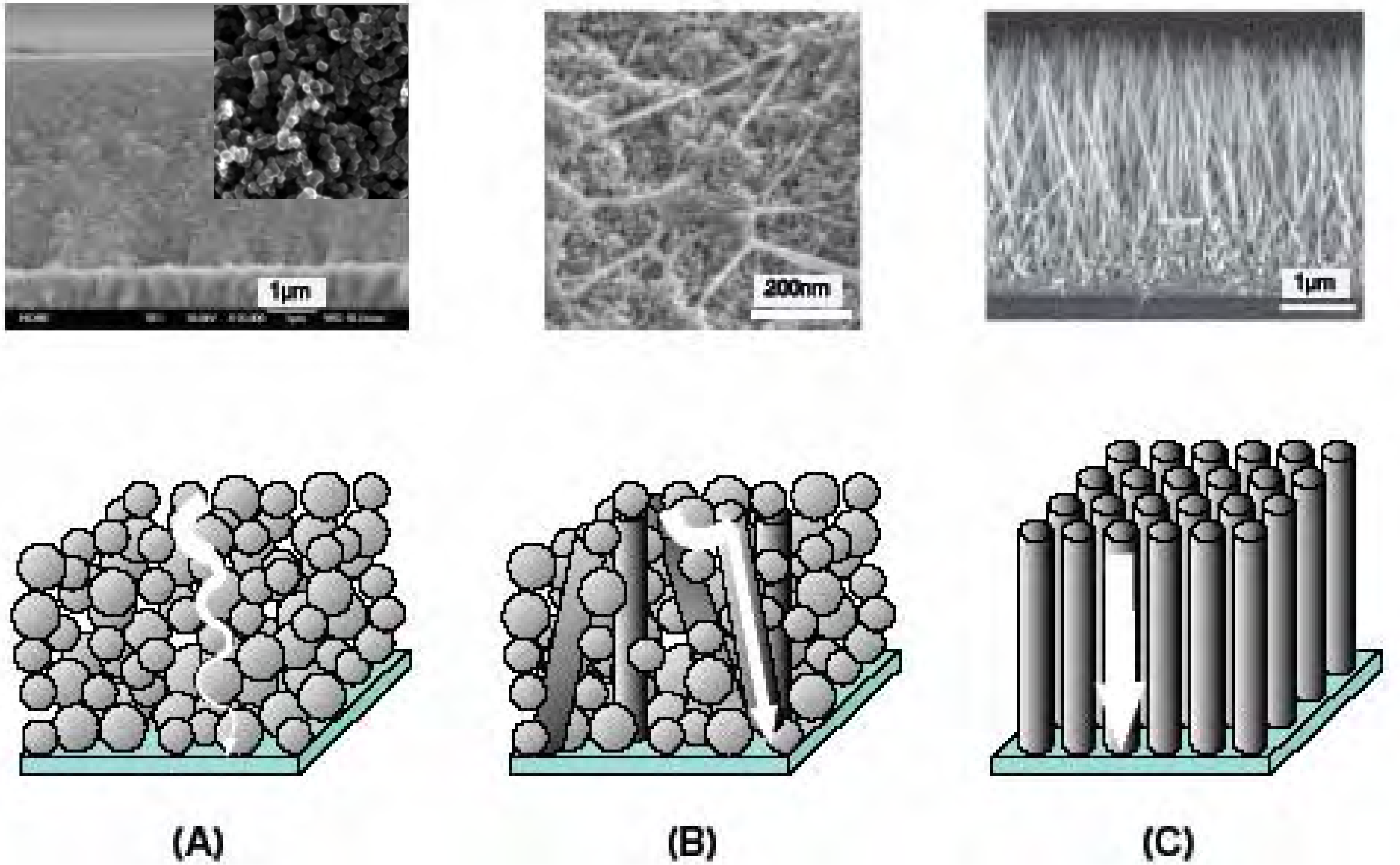


Prof. Y. Tsujii, *et al*, Institute for Chemistry, Kyoto Univ.

- Consept of supra-hierarchical nano-structured cell

Hybrid solar Cell

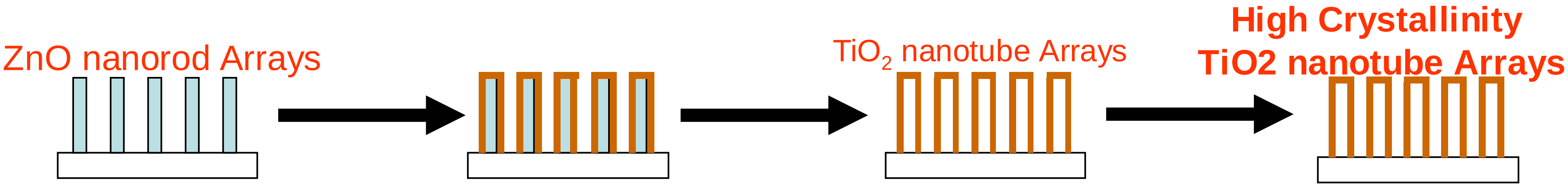
Introduction of 1D nano-materials for facile carrier path in the bulk hetero-junction

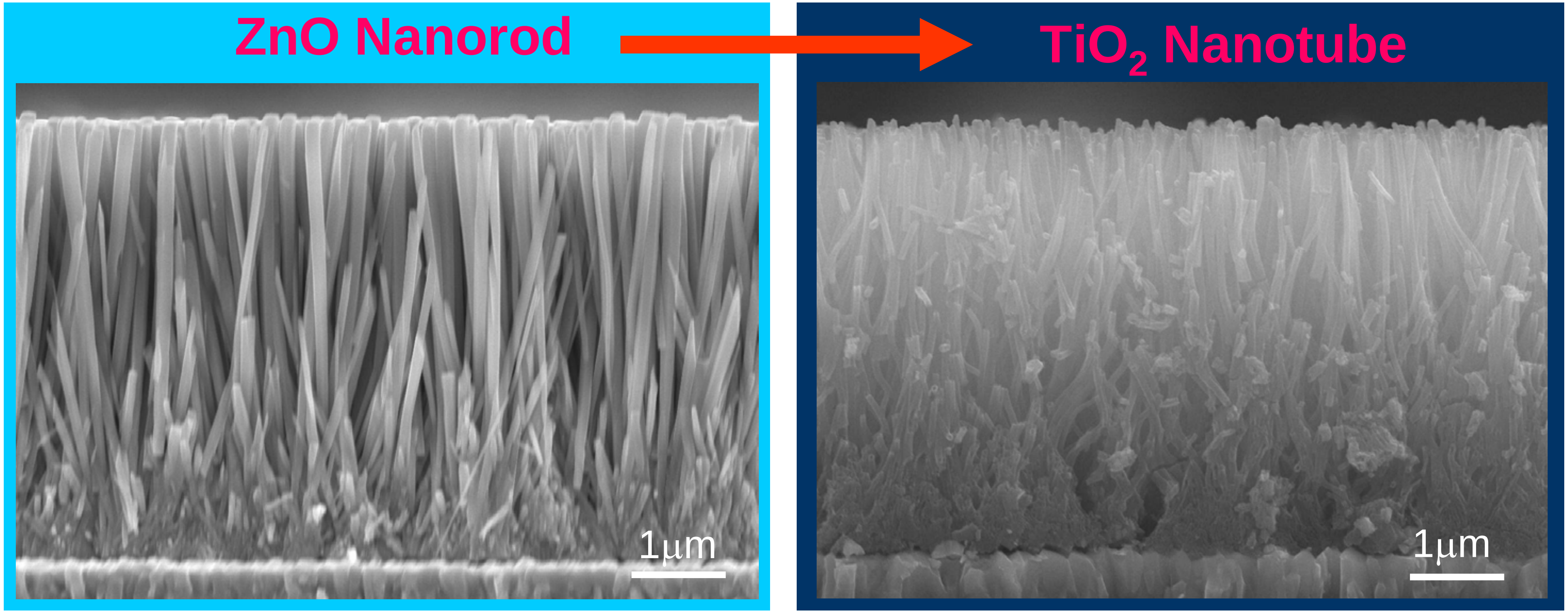


1st Generation **2nd Generation** **3rd Generation**

TiO_2 Nanotube Arrays

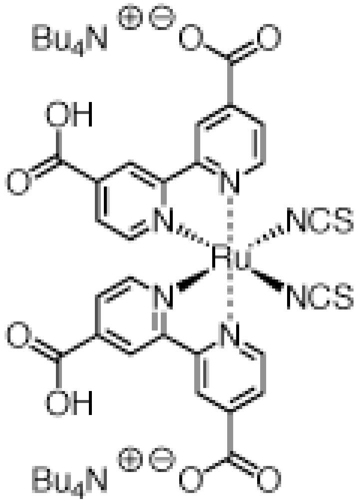
- **Fabricating TiO_2 nanotube array from ZnO nanorod array template**



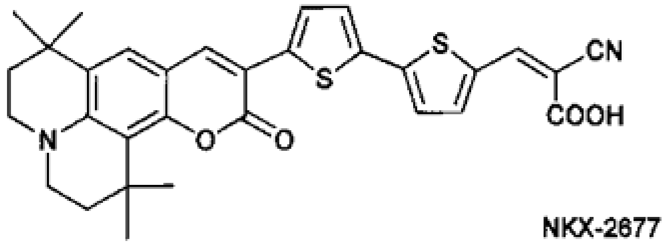


Enhance the performance of the nanorod structure of ZnO/ polymer hybrid solar cell by modifying the metal oxide surface with various dyes

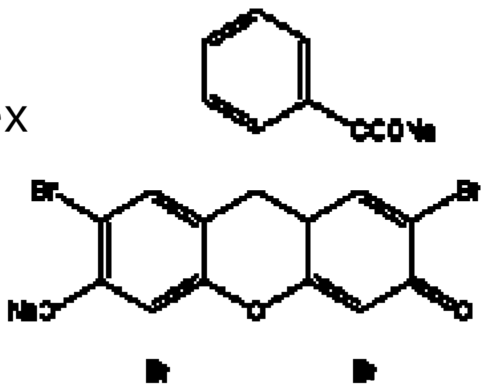
Concentration : 0.5 mM



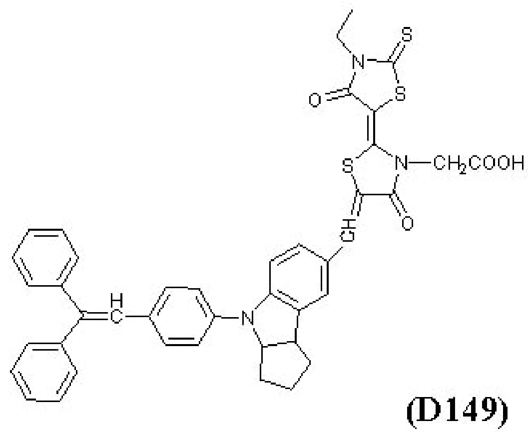
N719
Ruthenium complex



NKX-2677
Coumarin dye

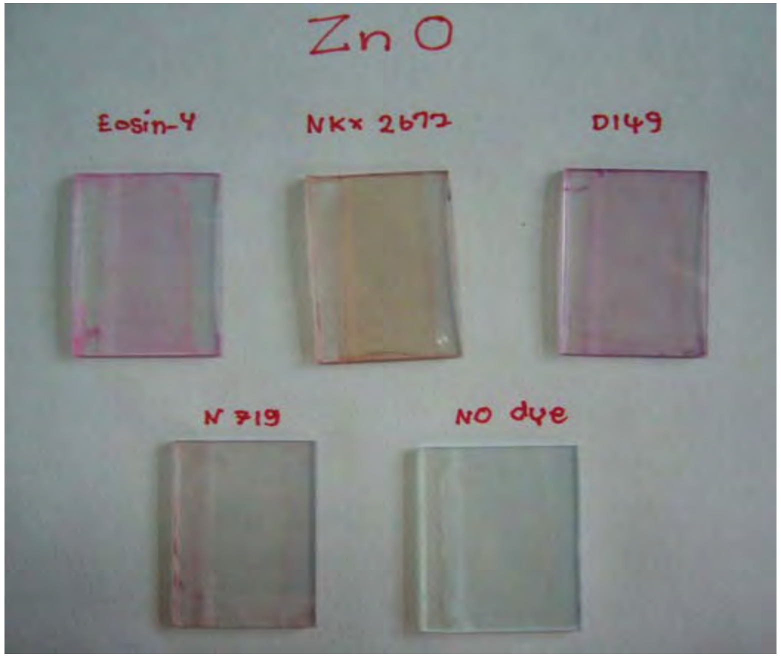


Eosin-Y
Xanthene dye

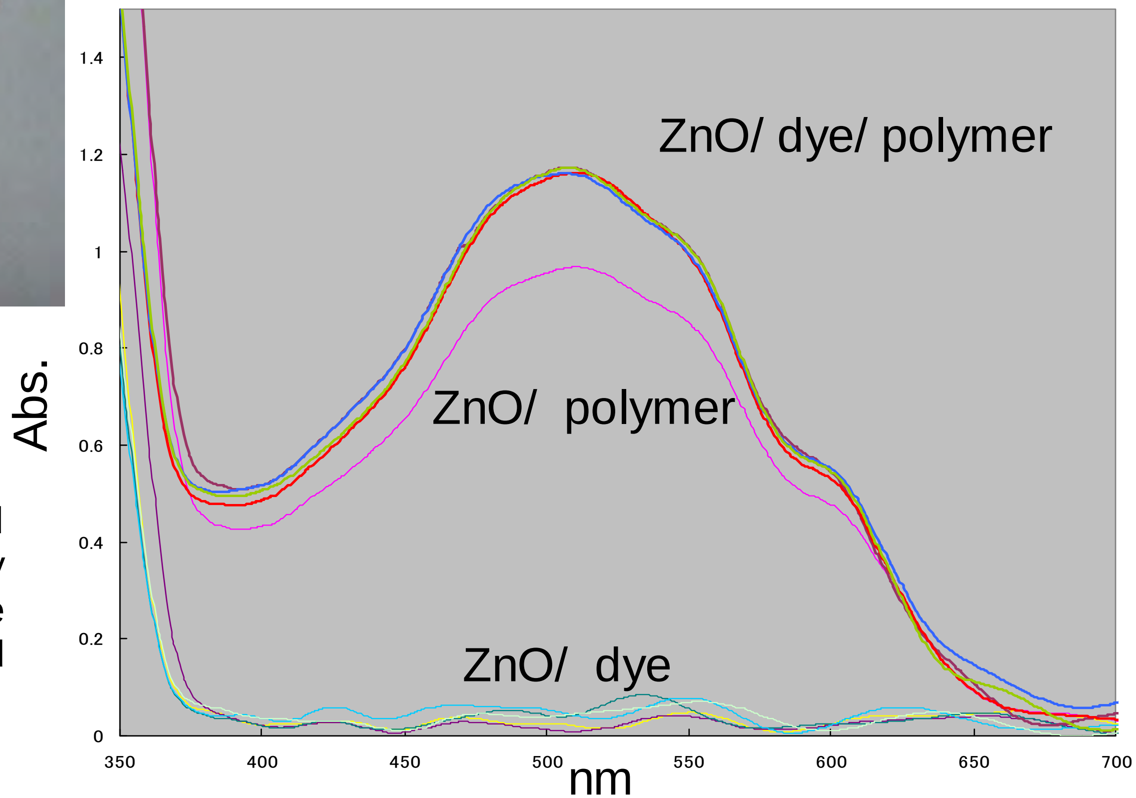


D149
Indoline dye

Enhance the performance of the nanorod structure of ZnO/ polymer hybrid solar cell by modifying the metal oxide surface with various dyes



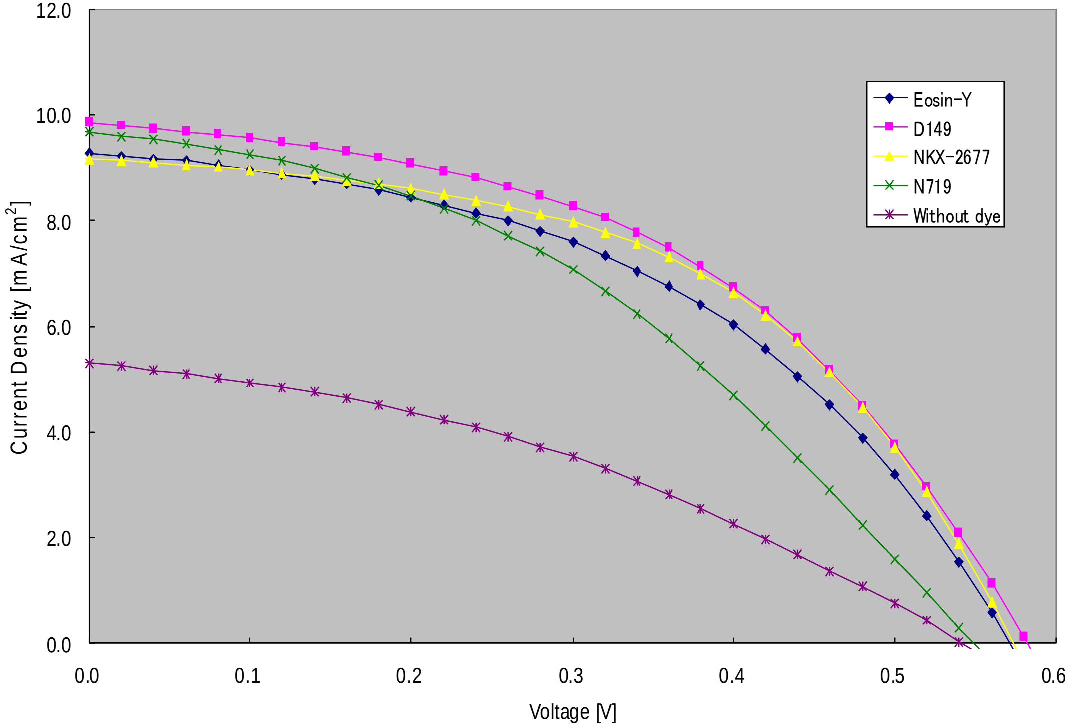
• The peaks of each dye can be observed before polymer deposition
• After dye treatment and polymer deposition, we can't observed any peaks of dye treatment



From UV result, the amount of coated active film after surface modification by dye was different to un-modified surface because the contact angle was changed after surface treatment

Enhance the performance of the nanorod structure of ZnO/ polymer hybrid solar cell by modifying the metal oxide surface with various dyes

Structure : FTO/ZnO/P3HT:PCBM/Ag

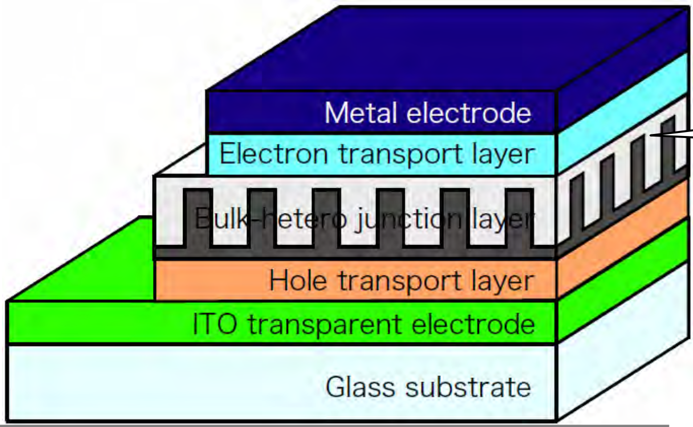


Polymer : P3HT:PCBM (30:18 mg/ml)
Speed of spinning : 1000 rpm
Anealed : 140 ^oC 5 min
Electrode : Ag

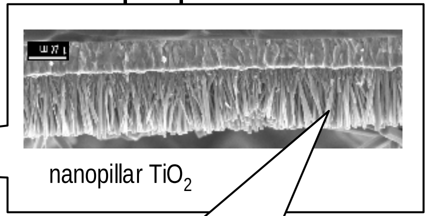
dyes	n [%]	FF	Voc[V]	Jsc[mA/cm2]
Eosin-Y	**2.43**	0.46	0.57	9.28
D149	**2.71**	0.47	0.58	9.87
NKX-2677	**2.63**	0.48	0.58	9.57
N719	**2.13**	0.4	0.55	9.68
Without dye	**1.06**	0.37	0.54	5.29

- The significantly improve in performance of device after dye treatment
- Surface treatment with ruthenium dye (N719) show the low FF value compared to other dyes
- Surface treatment with D149 show the high performance in Jsc of 9.87 mA/cm^2, Voc of 0.58V, FF of 0.47, and η of 2.71%

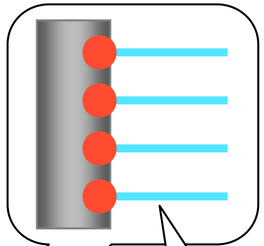
Supra-hierarchical nano-structured cell

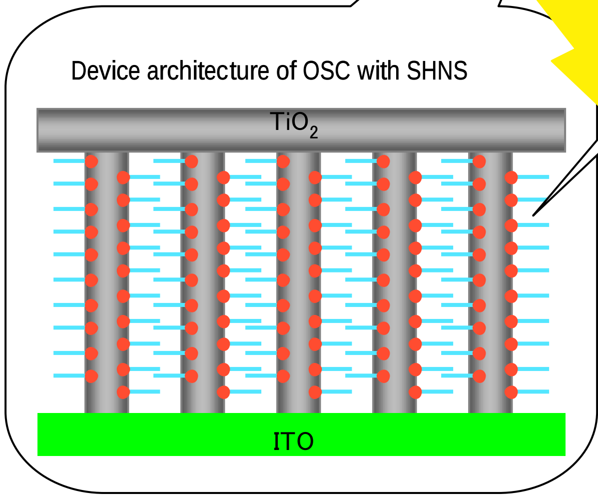


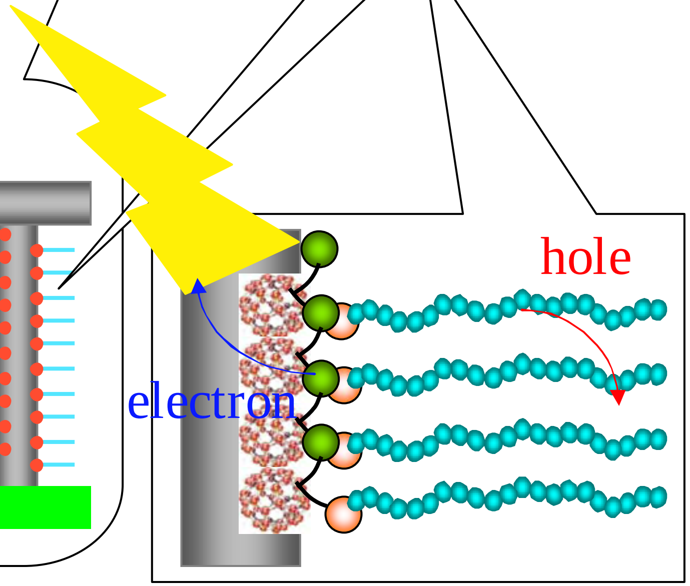
（proposal１）



（proposal ２）







（initiator or linker-D-A type）methanofullerene

Power conversion efficiencies

$$\eta_{EQE} = \eta_{A} \times \eta_{ED} \times \eta_{CT} \times \eta_{CC}$$

$$\eta \propto \Delta E_g \times \mu \times L \times \int \varepsilon \, d\lambda$$

ΔE_g : HOMO (Donor) and LUMO (Acceptor) offset

μ: carrier mobility

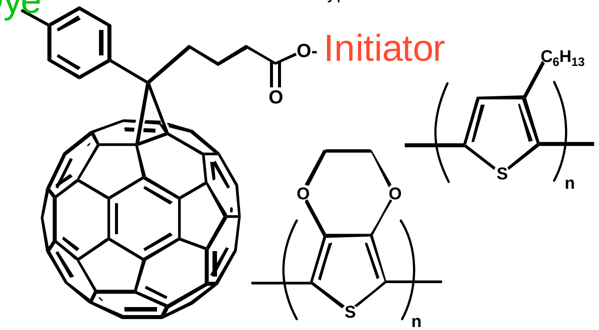
L : exciton diffusion length

ε : absorbance

λ : wavelength

- Charge separation efficiency → up
- Lifetime of exciton → long
- Charge transport efficiency → up
- Large absorption coefficient →IPCE up

Binder & Dye



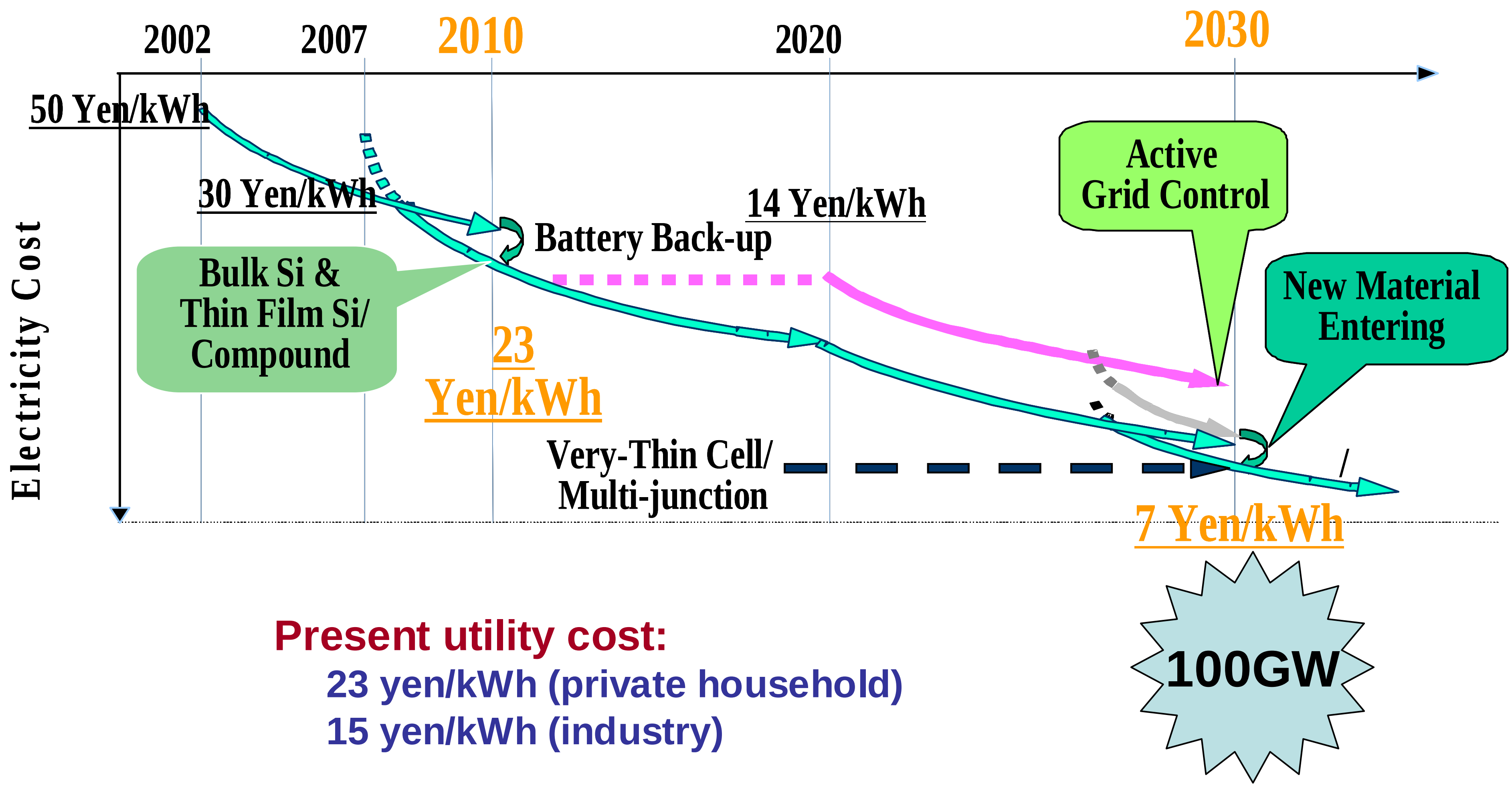
Orientation controlled graft polymerization of thiophenes from methanofullerene on TiO_2 electrode

（prospects for upconversion）

$$\eta = V_{oc} \times J_{sc} \times FF$$

$$= 4.1\% \times 0.8/0.6 \times 13/10 \times 0.7/0.7 > 7.1\%$$

Japanese PV Roadmap until 2030



Present utility cost:

23 yen/kWh (private household)
15 yen/kWh (industry)

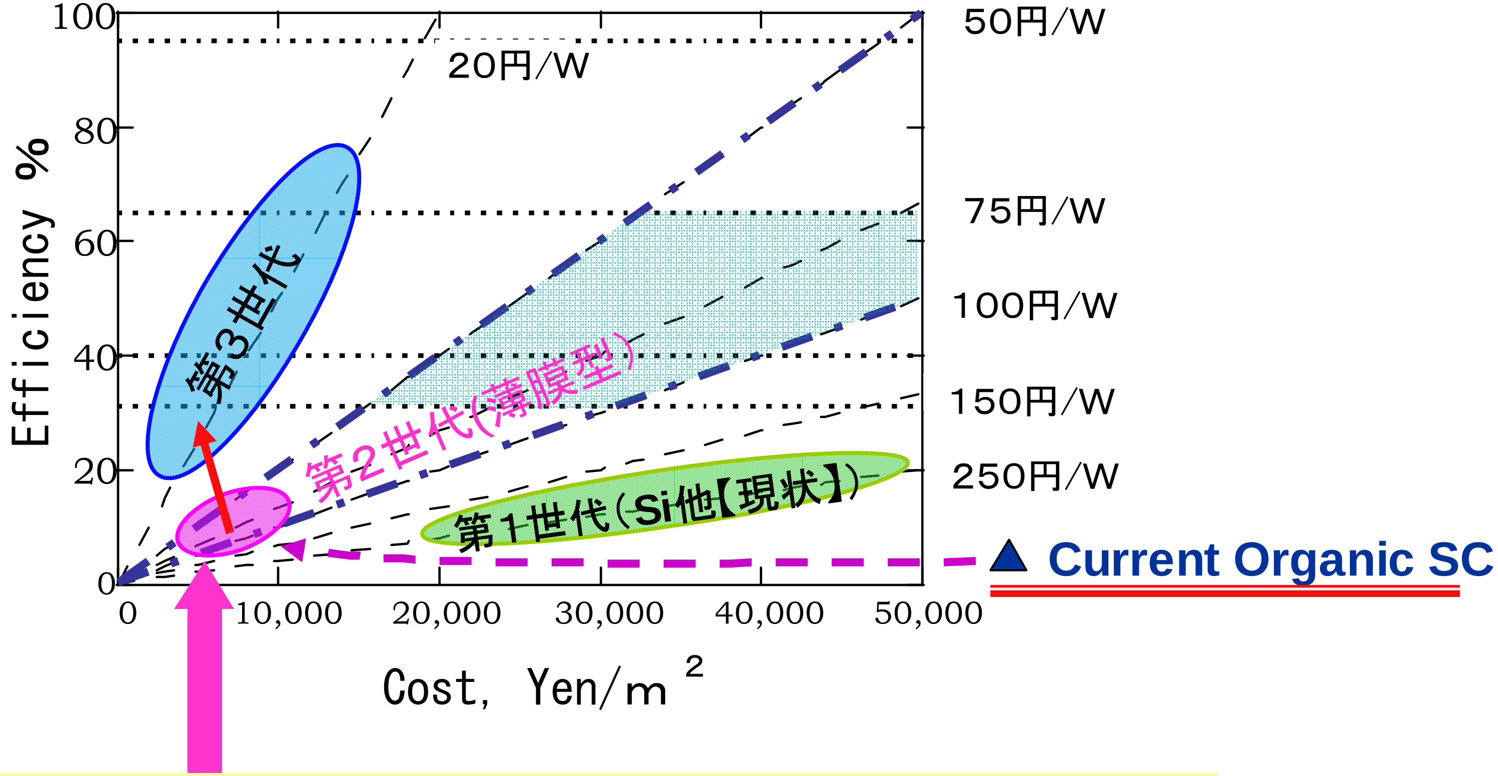
Electricity generation cost:

5-6 yen/kWh (Nuclear)
9 yen/kWh (hydro)

1US$= 113 JPY

1THB= 3 JPY

Research Target：Organic Solar Cell for Roof Top Module



2nd Generation（low cost）for Market Application
3rd Generation (high efficient) for Long Target

1st Target【Year 2015】

Module effic.： 10 %
Cell Cost： 75Yen／W
Power Cost： 14Yen／kWh