# Synthesis of ZnO Nano/Microspheres and Development of Organic Solar Cells

**Gon Namkoong**
**ARC-Old Dominion University**

# Outline

- **Synthesis of ZnO nano/microspheres**
  - ✓ Control of ZnO morphologies
  - ✓ Effect of structure direct agents on ZnO morphologies
  - ✓ Control of uniformity, distribution, and size of ZnO spheres
- **Organic solar cells**
  - ✓ Recombination process of organic solar cells
  - ✓ Degradation mechanisms of organic solar cells
  - ✓ Simulation of 3D organic morphologies
- **Power of Words**

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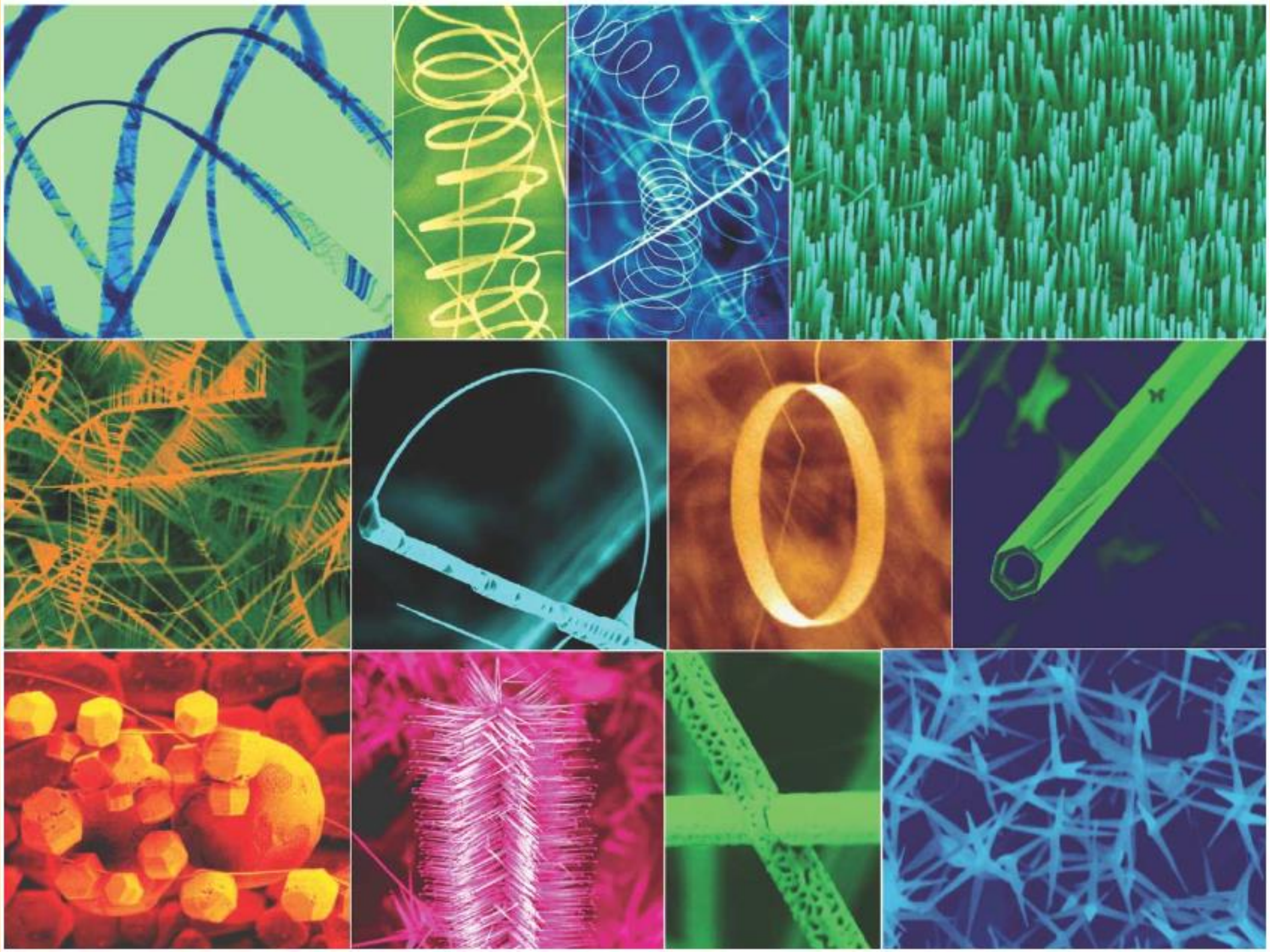
- **Power of His Words**

# ZnO morphologies

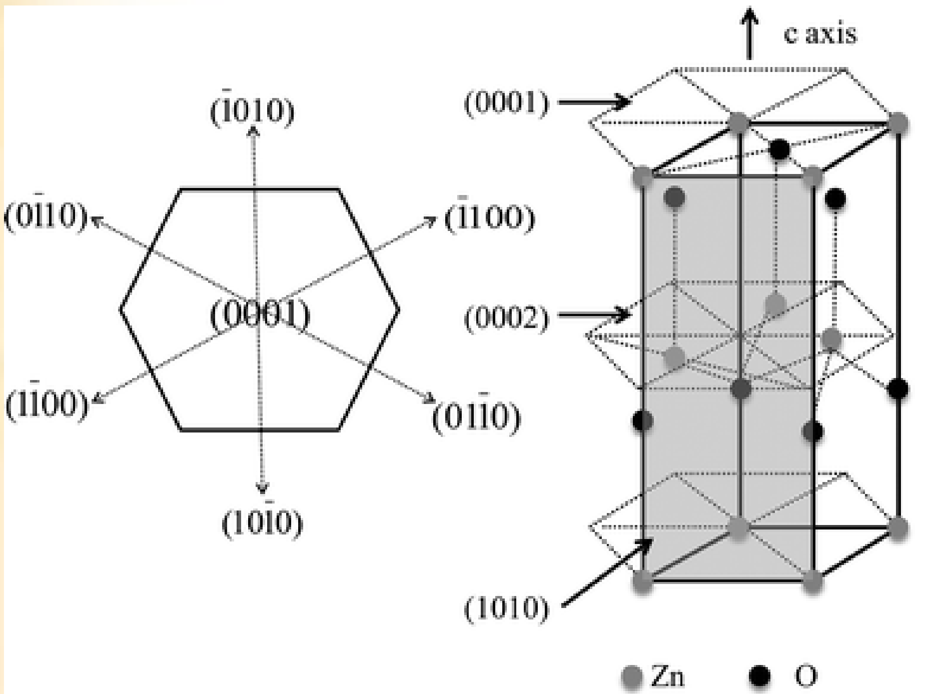


Unique optical, electrical, and structural properties
$\Rightarrow$ Many applications

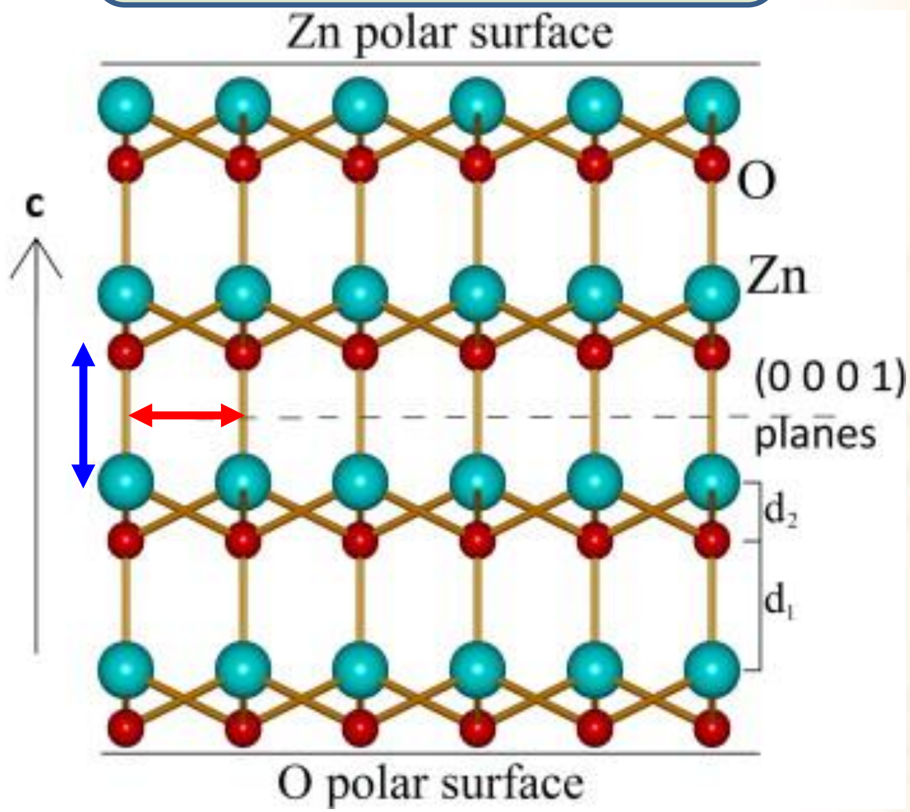
Missing morphology
$\Rightarrow$ ZnO sphere

Materialtoday, Vol 7, p 26 (2004)

# ZnO structures




Noncentrosymetric ZnO structure



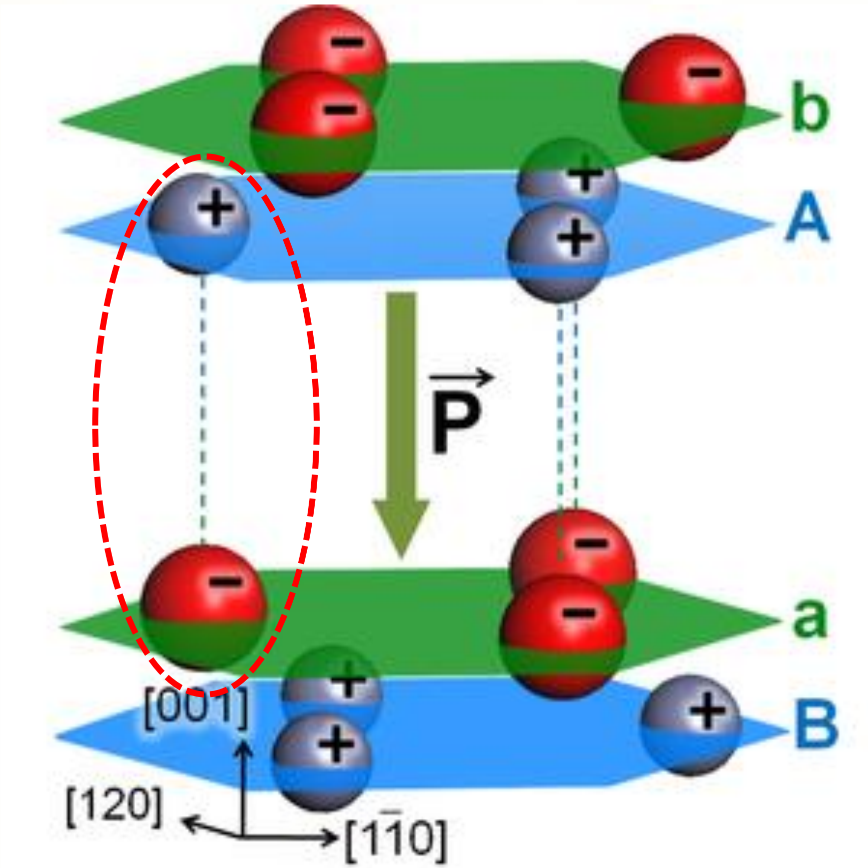

Nuclear Instruments and Methods in Physics Research Section B. Vol. 281, pp 77 (2012)

a=3.247 Å

b=5.207 Å

$$\frac{b}{a}=1.6$$

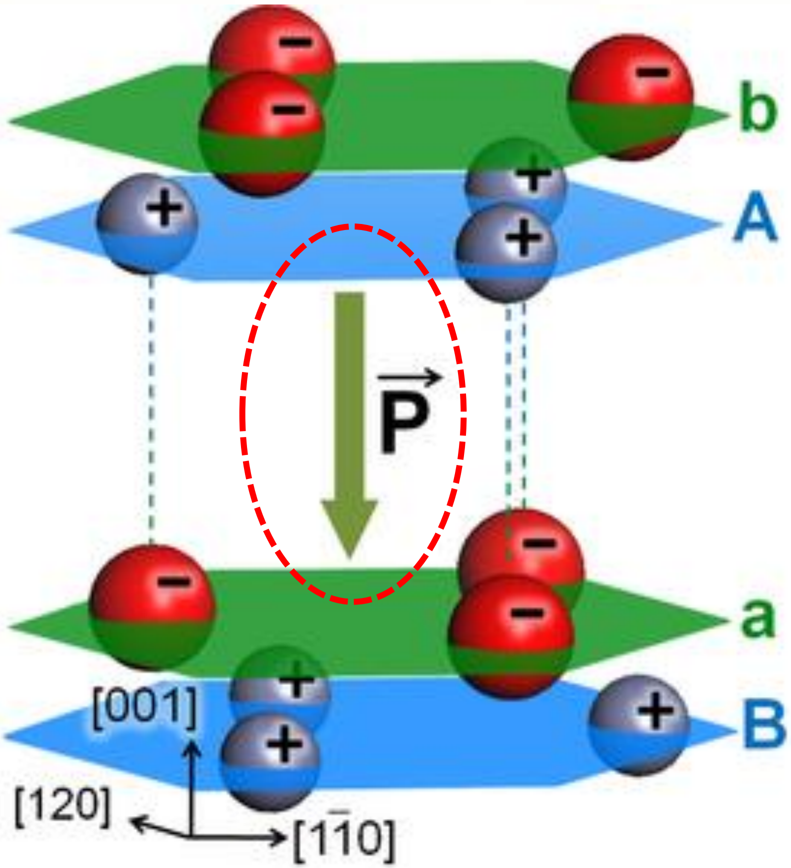
# ZnO structures (Cont.)




Scientific reports, Vol 2, pp 587

ZnO has a noncentrosymmetric crystal structure

# ZnO structures (Cont.)

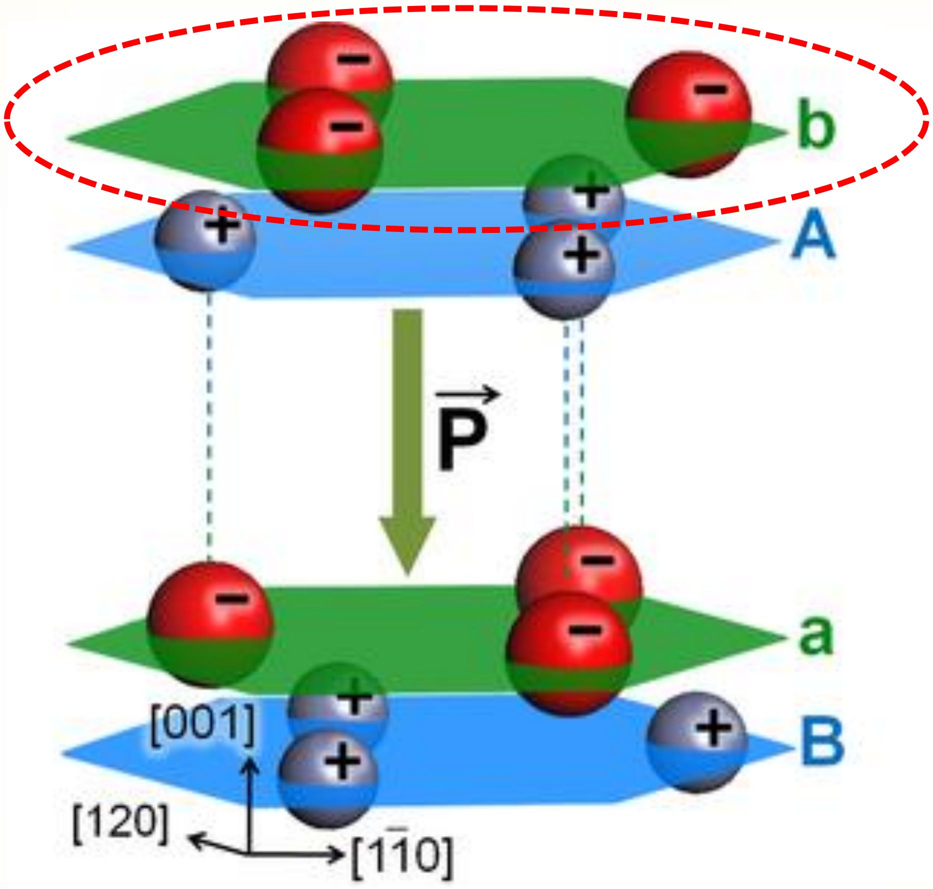



Scientific reports,
Vol 2, pp 587

ZnO has a noncentrosymmetric crystal structure

Strong spontaneous polarization

# ZnO structures (Cont.)




Scientific reports, Vol 2, pp 587

ZnO has a noncentrosymmetric crystal structure

↓

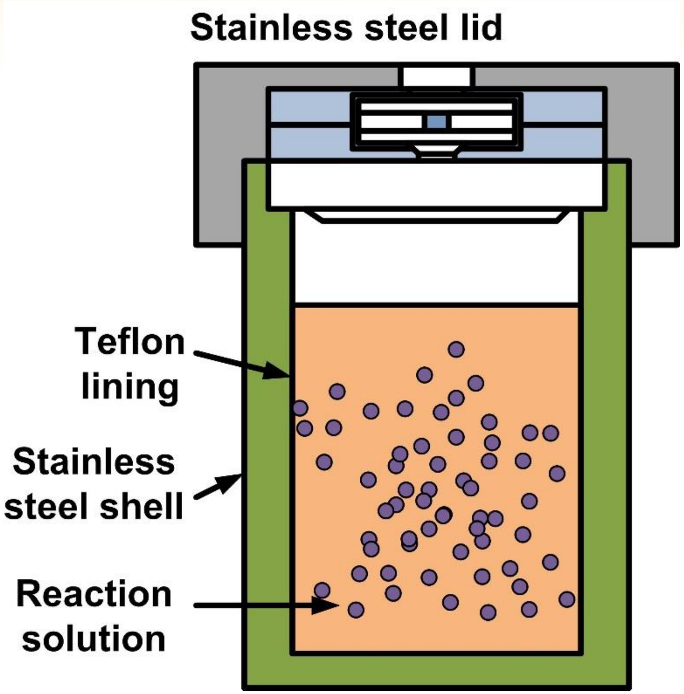
Strong spontaneous polarization

↓

Surface charge on the (0001) plane

# Hydrothermal synthesis of ZnO

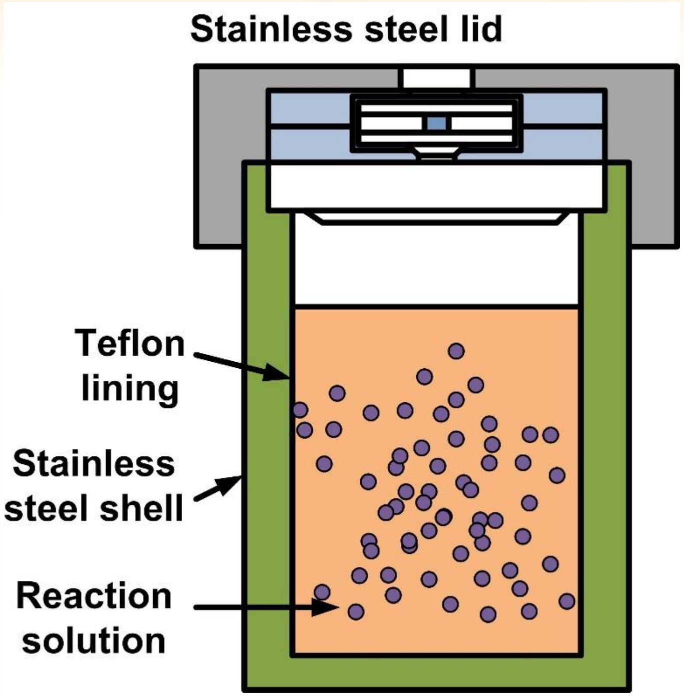
Autoclave reactor



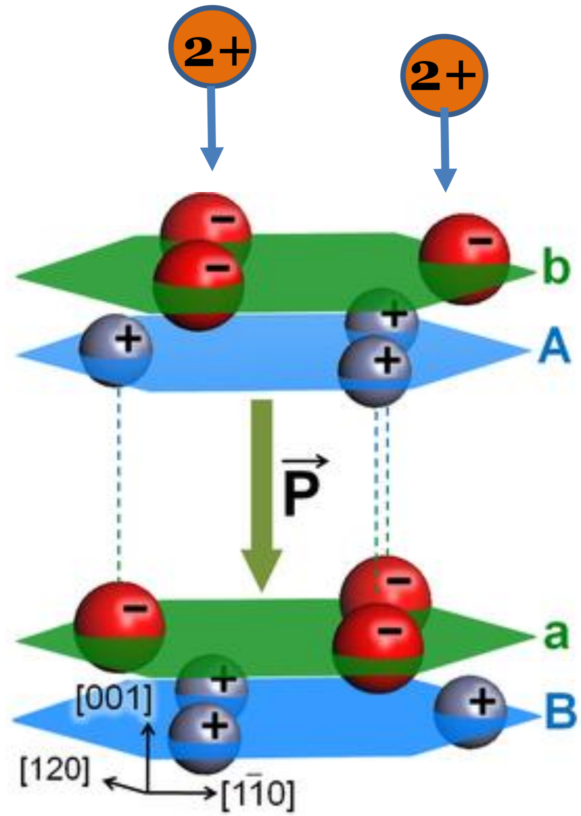

Zinc acetate $Zn((CH_3COO)_2 \cdot 2H_2O)$

Ammonia hydroxide $NH_4OH$

# Hydrothermal synthesis of ZnO




$Zn(NH_3)_4^{2+}$



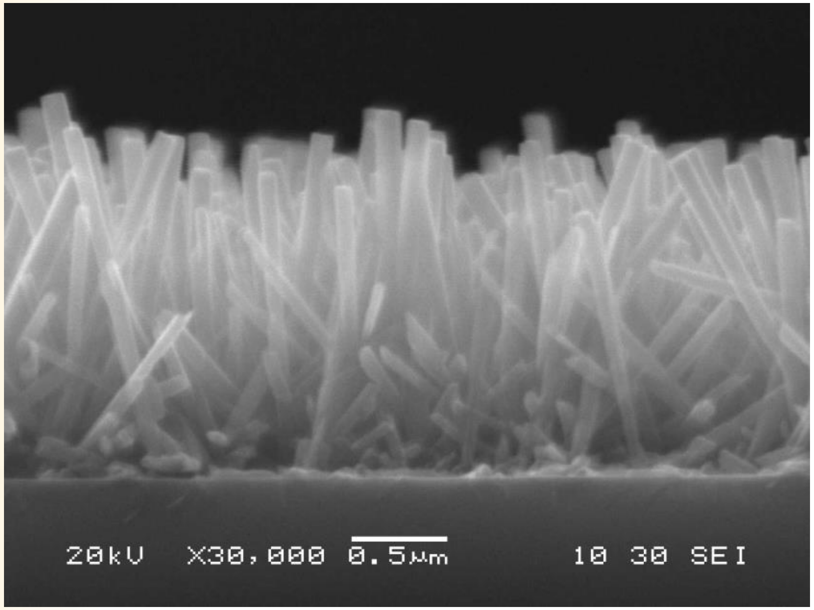

Zn cation $Zn(NH_3)_4^{2+}$

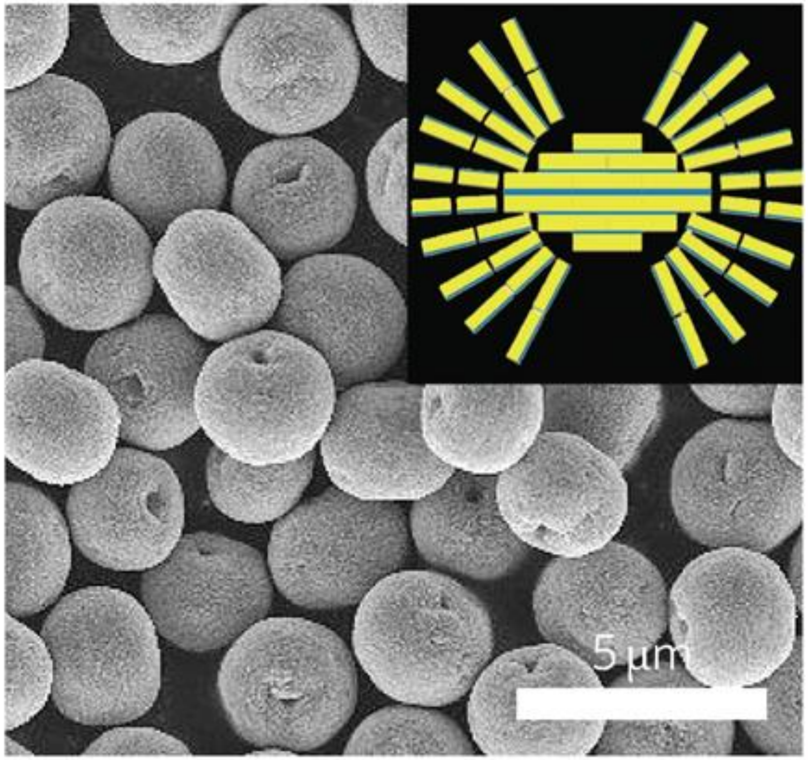
Zn anion $Zn(OH_3)_4^{2-}$

Scientific reports, Vol 2, pp 587

# Hydrothermal synthesis of ZnO

**Preferred growth of ZnO**

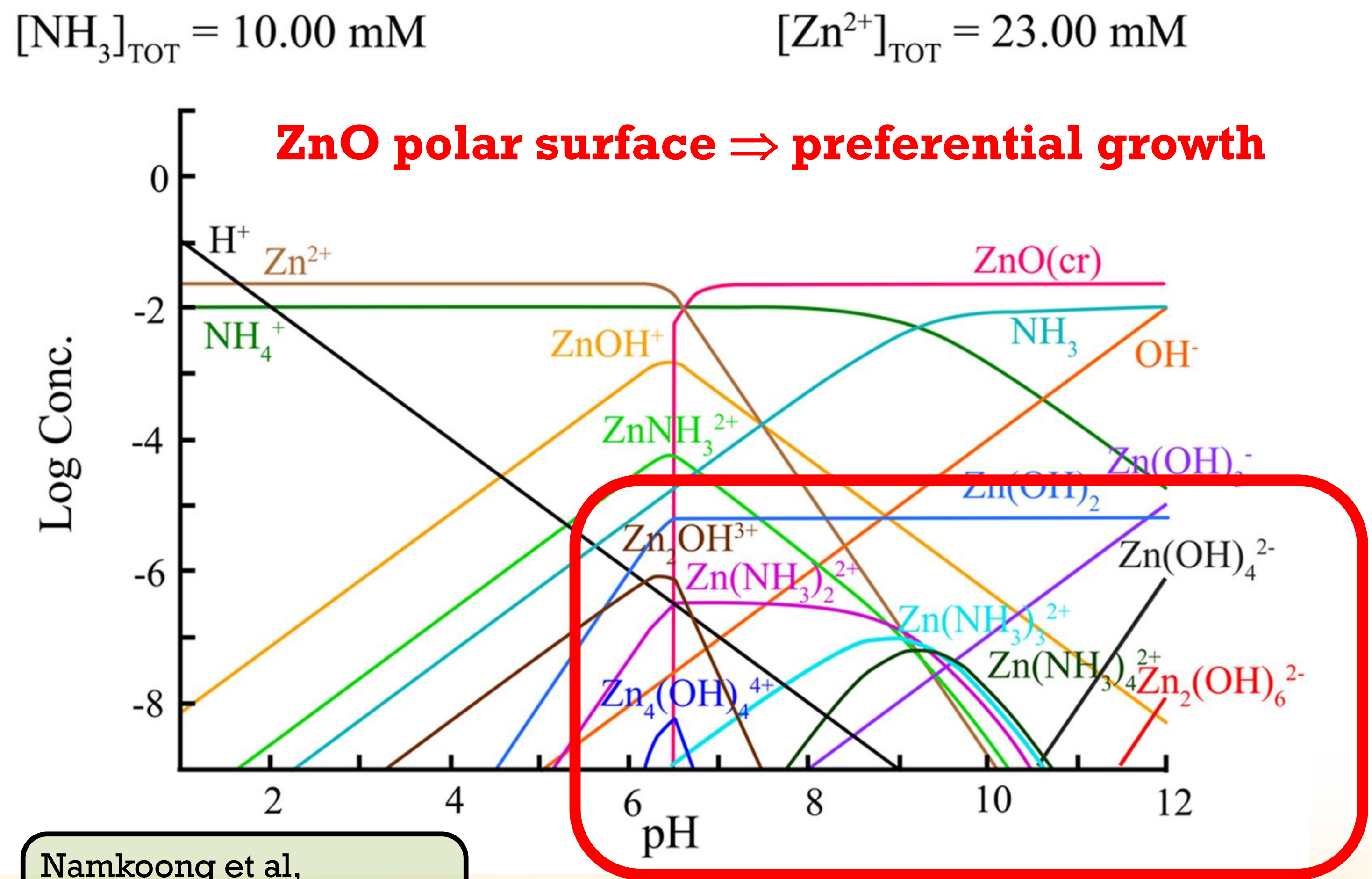



Nature nanotechnology, Vol. 6, pp 103 (2011)

# Novel approach for ZnO spheres

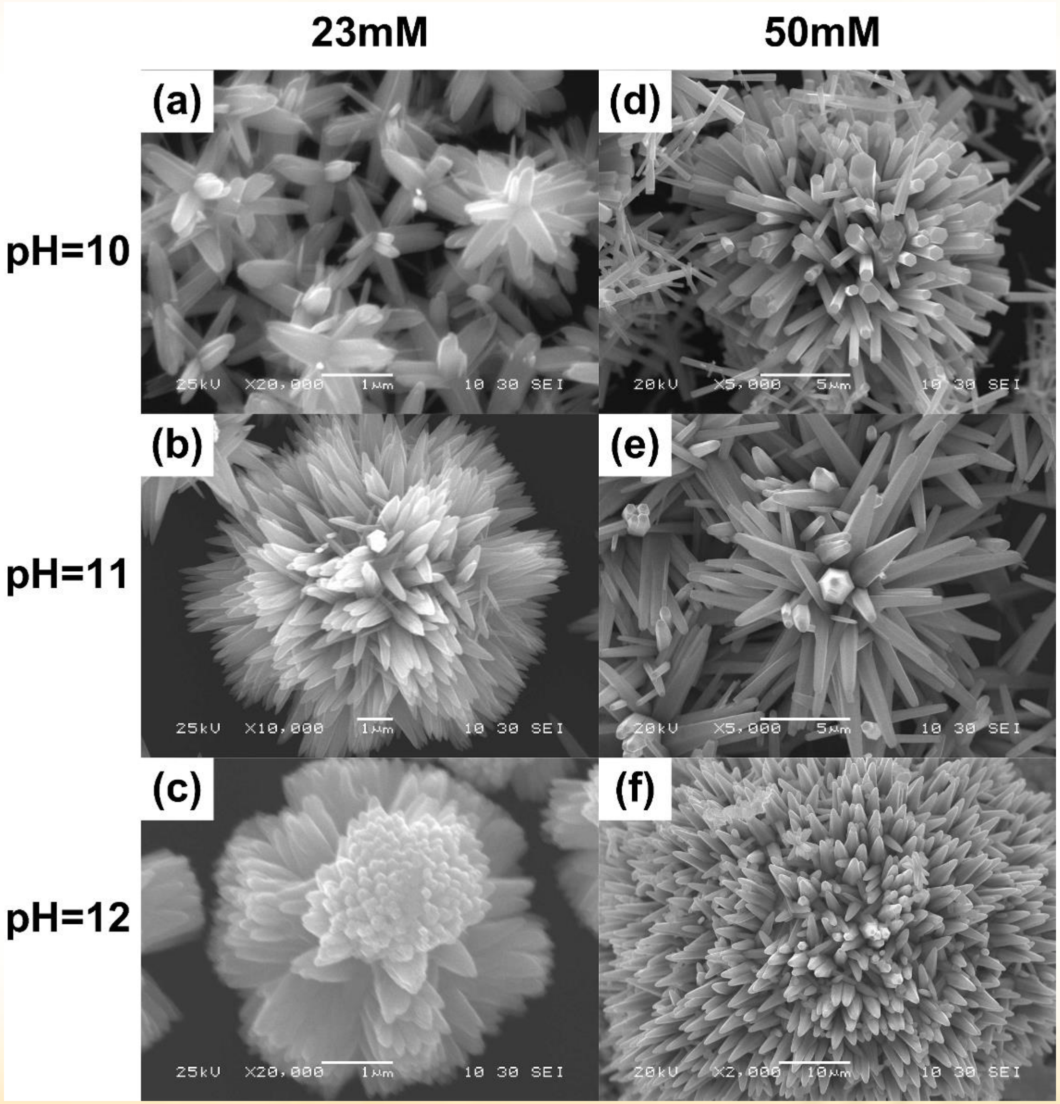
1. Control of cation species ⇒ adjustment of pH




Namkoong et al,
Thin Solid Films, Vol. 534,
pp 76 (2013)

# ZnO with different pH values

Zinc acetate

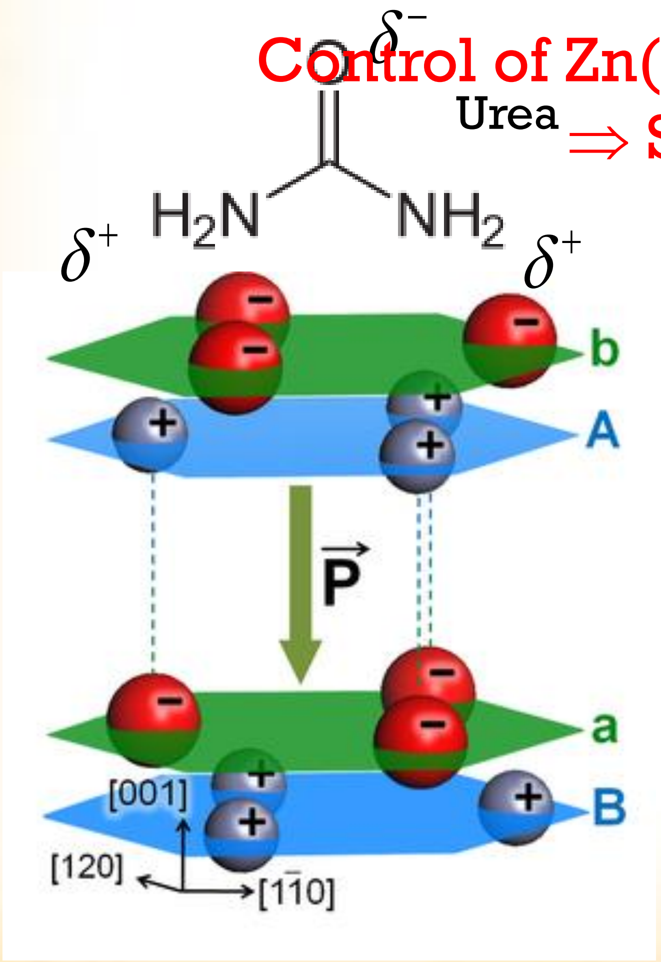


# Novel approach for ZnO spheres

2. Passivate the polar surface using SDA

Control of $Zn(NH_3)_4^{2+}$ nucleation species

$\Rightarrow$ Spherical shape




Structure directing agents (SDA)– Urea and ethanol

↓

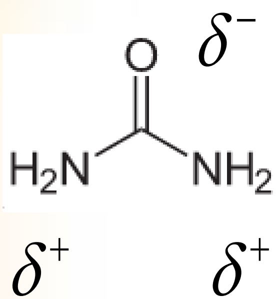
SDA will passivate ZnO that suppress further nucleation

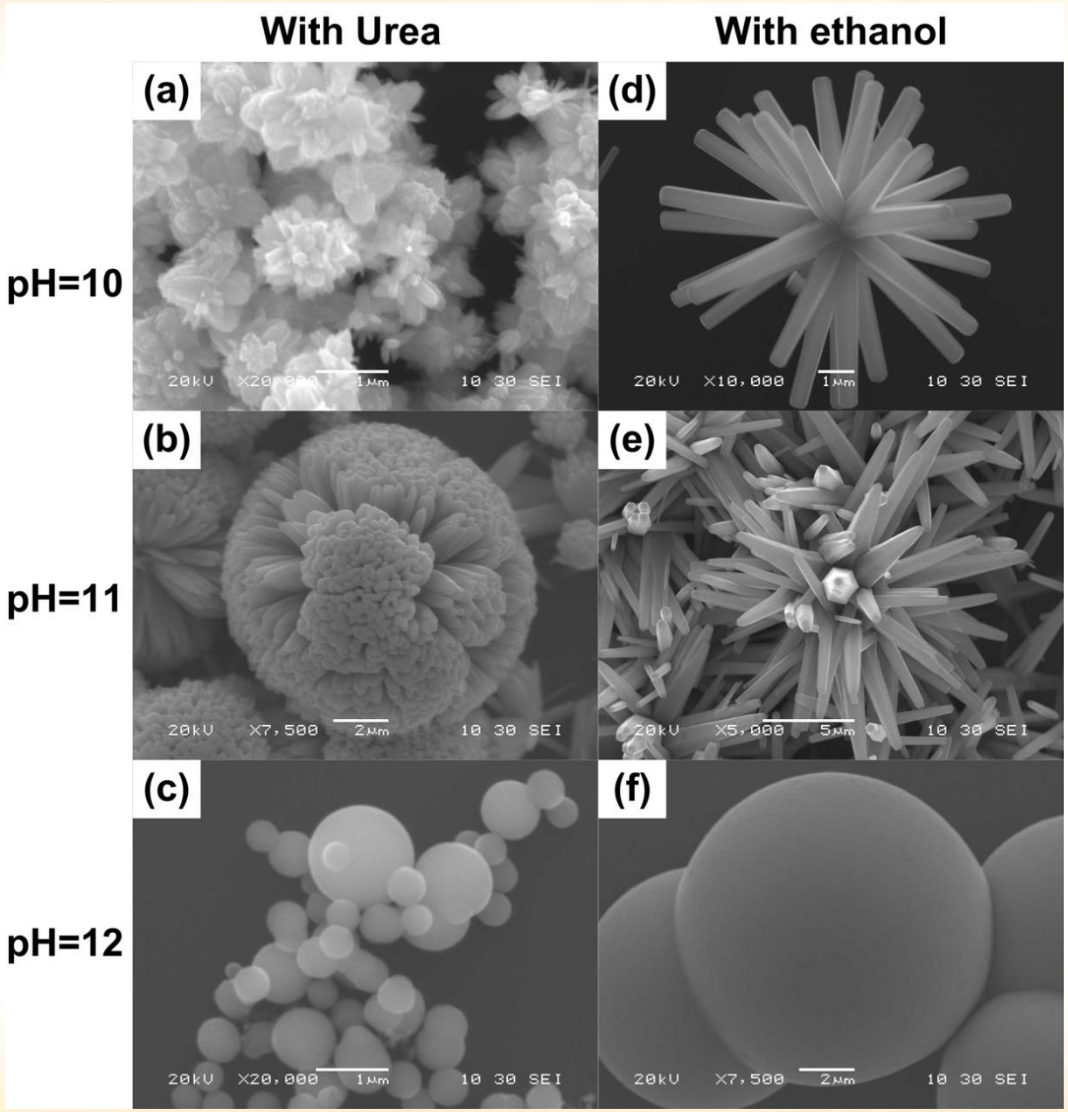
↓

Suppression of (0001) growth

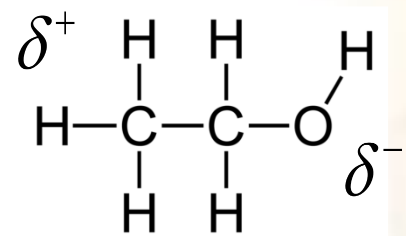
# Effect of SDA on ZnO morphologies

**Urea**

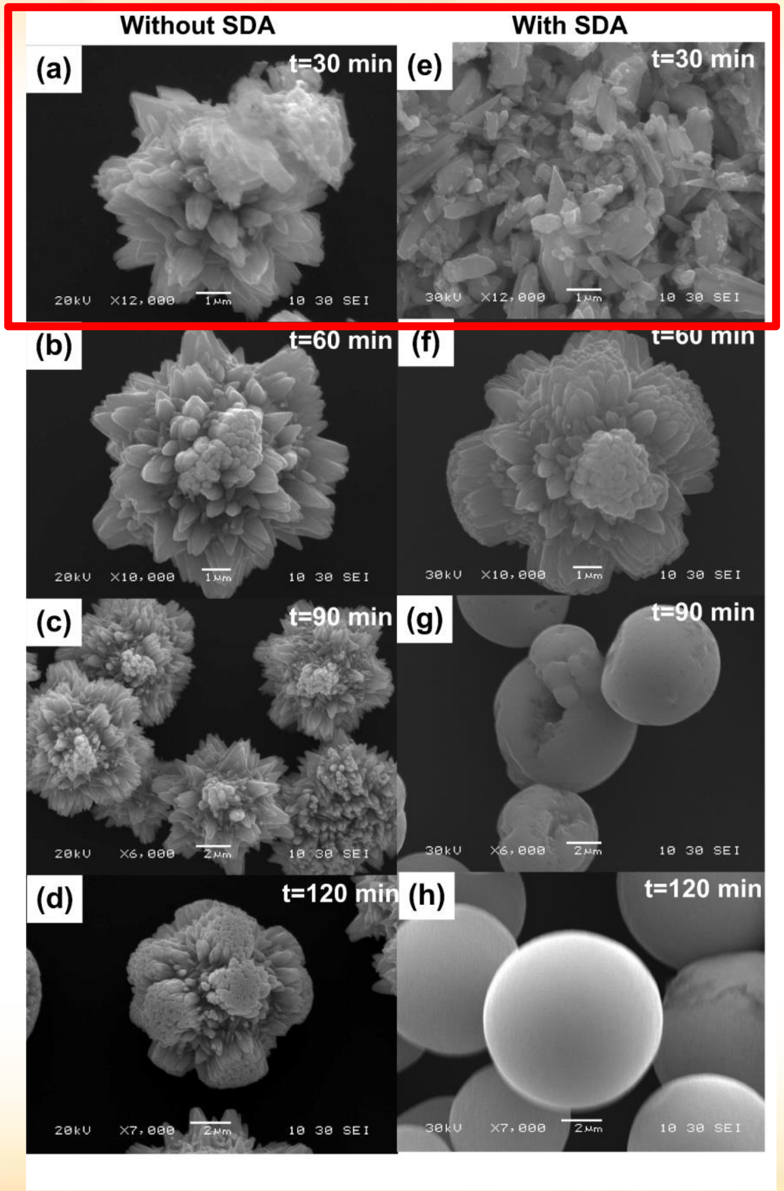



**ethanol**



# Temporal evolution of ZnO



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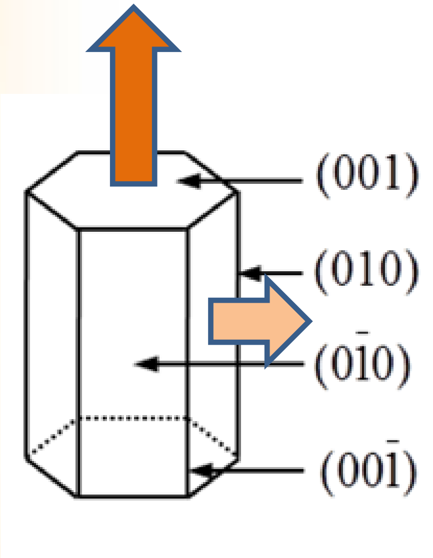


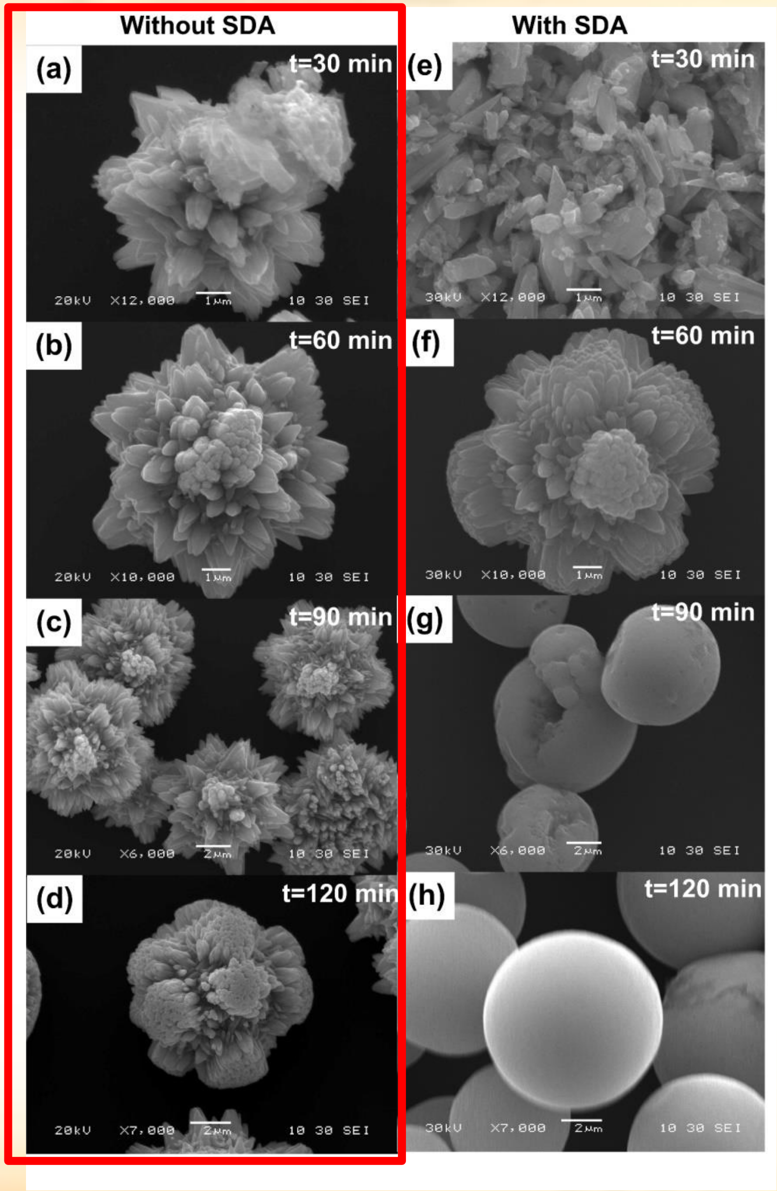

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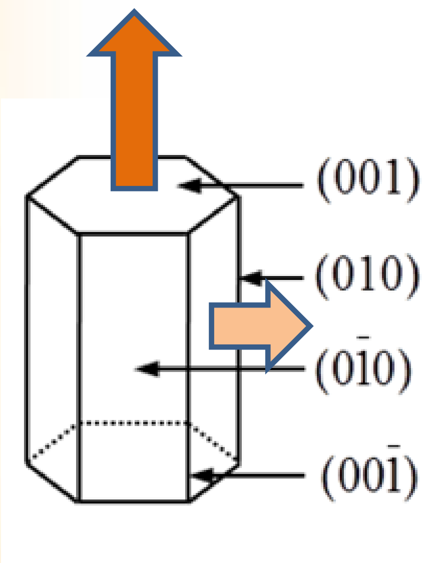
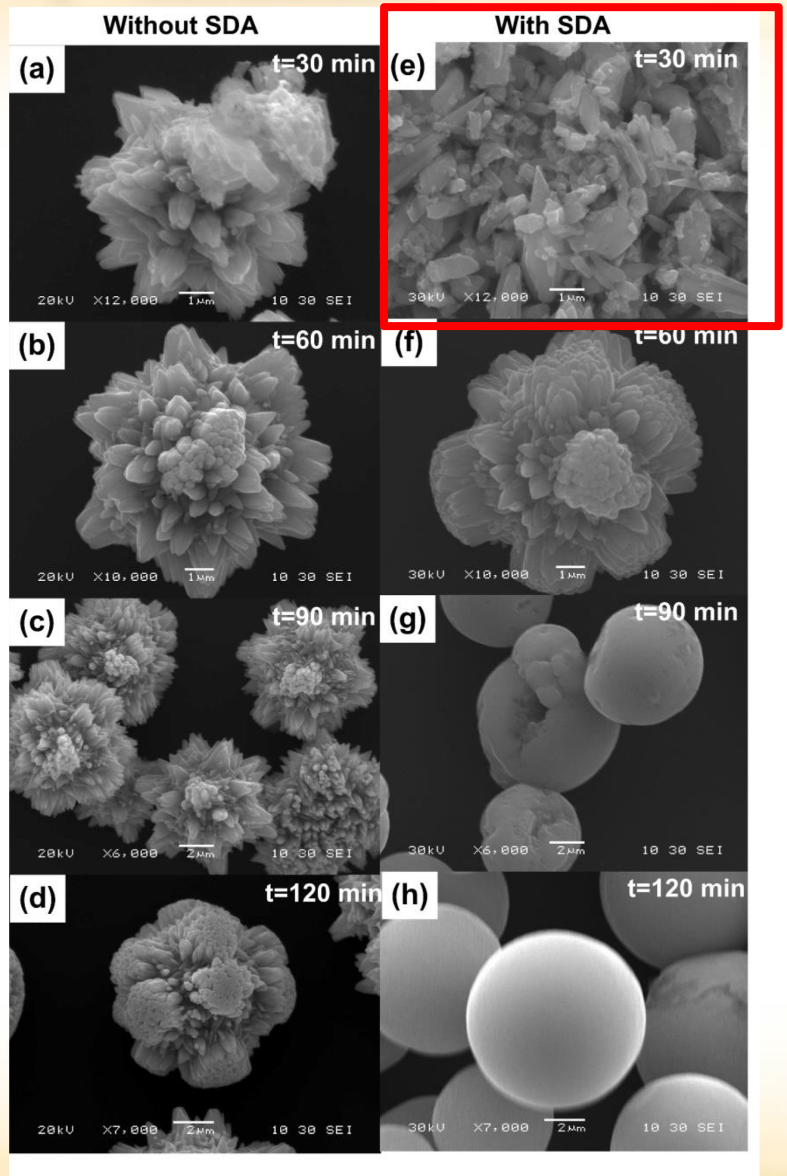
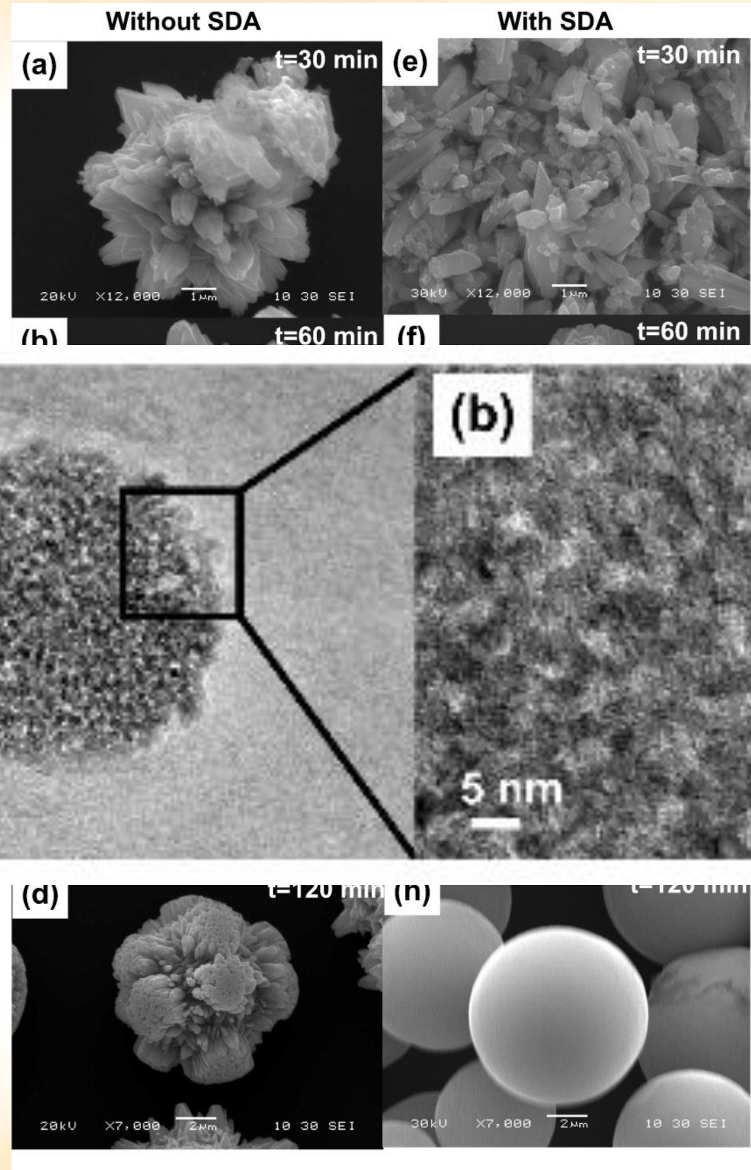
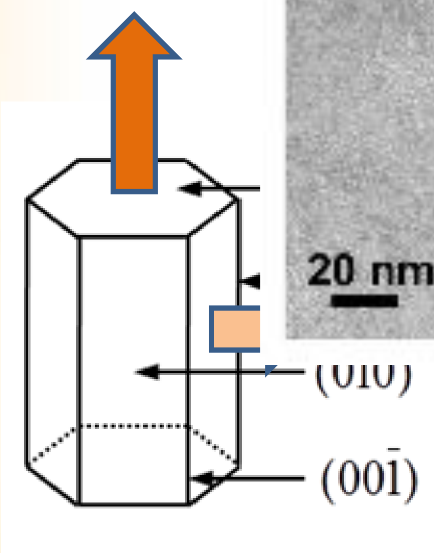
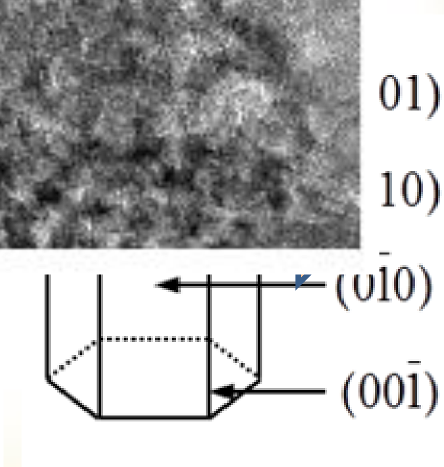


# Temporal evolution of ZnO

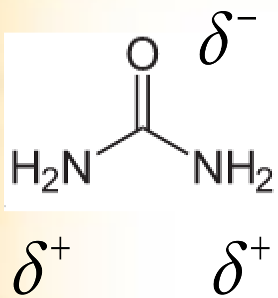


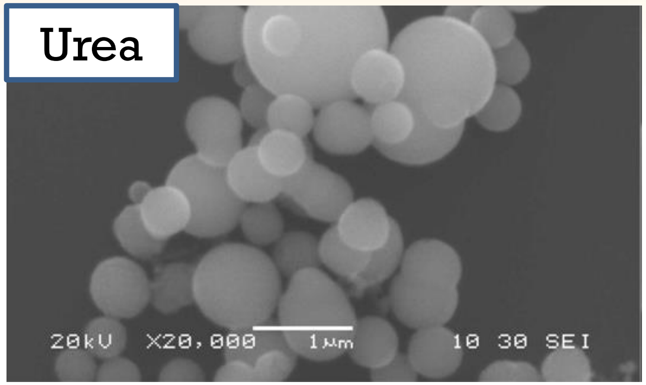



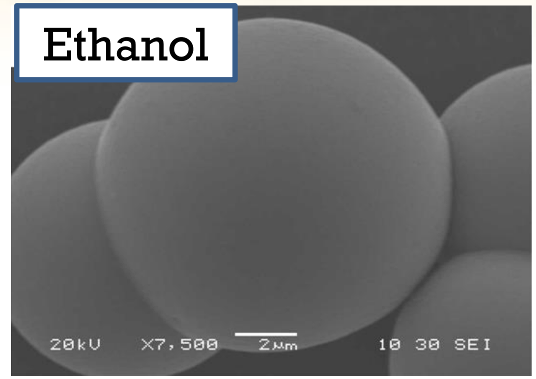



# Control of size and distribution of ZnO spheres

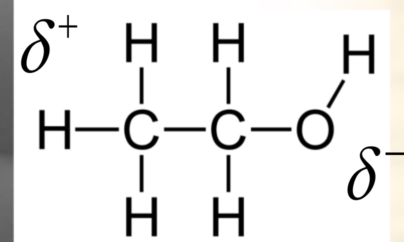
**Urea**



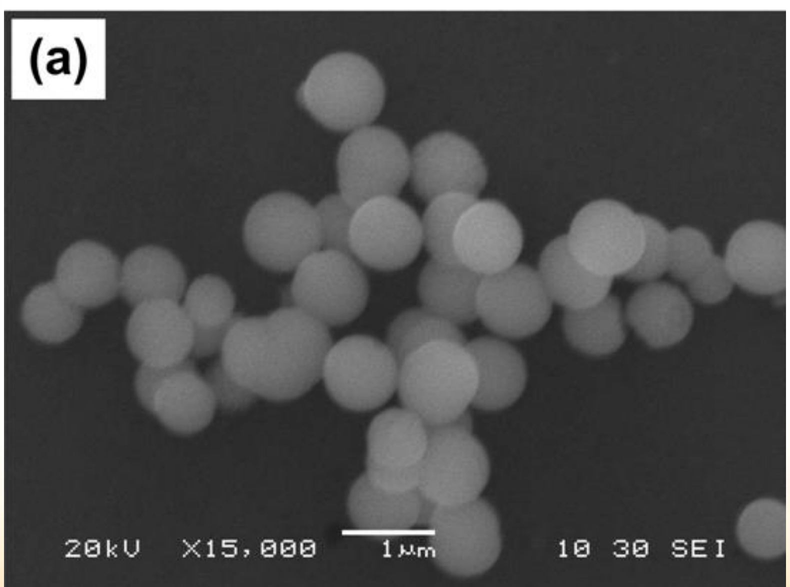



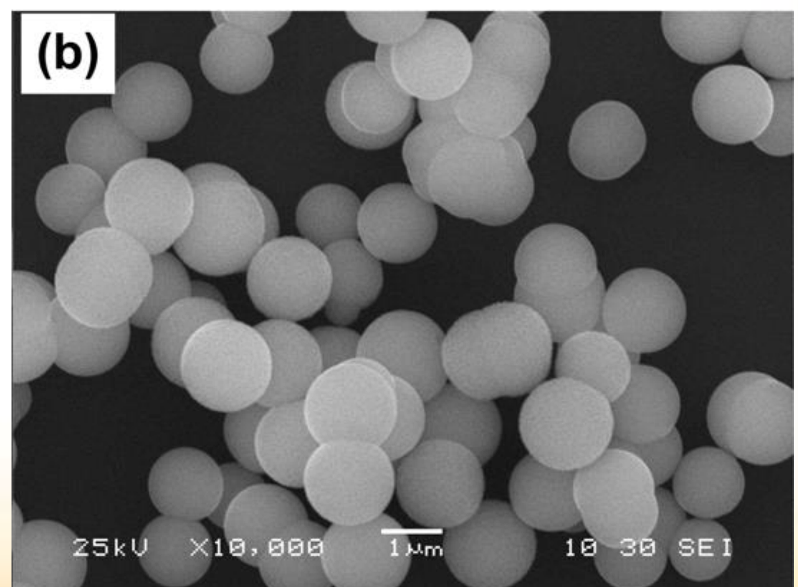

**ethanol**



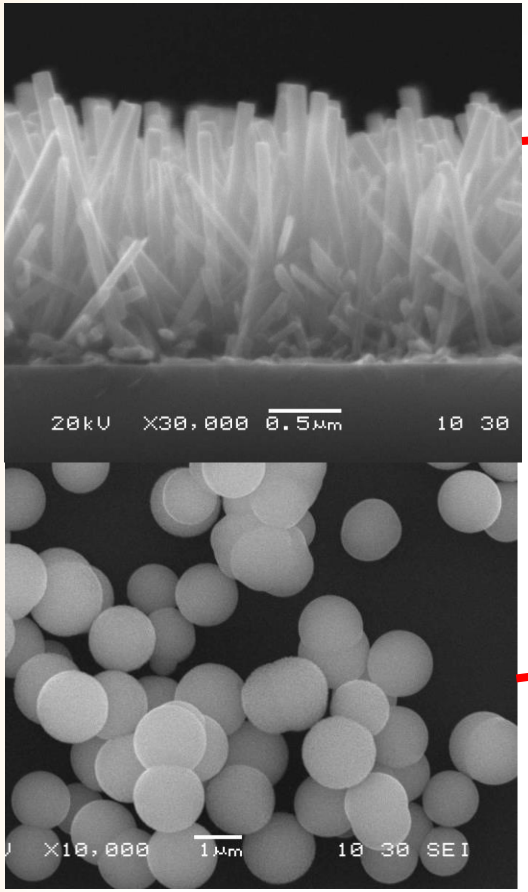

**Urea (1):Ethanol (1)**

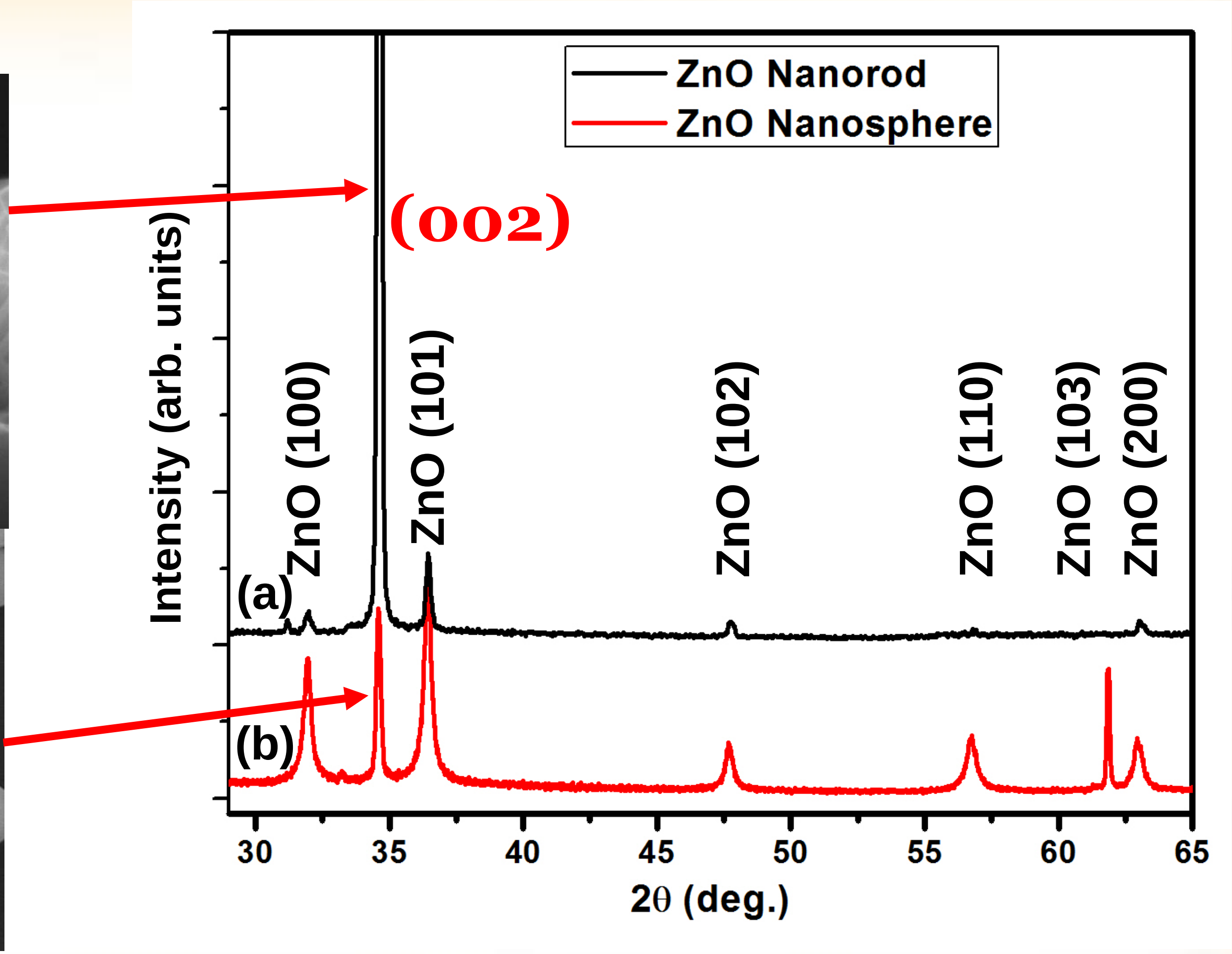



**Urea (1):Ethanol (1.25)**



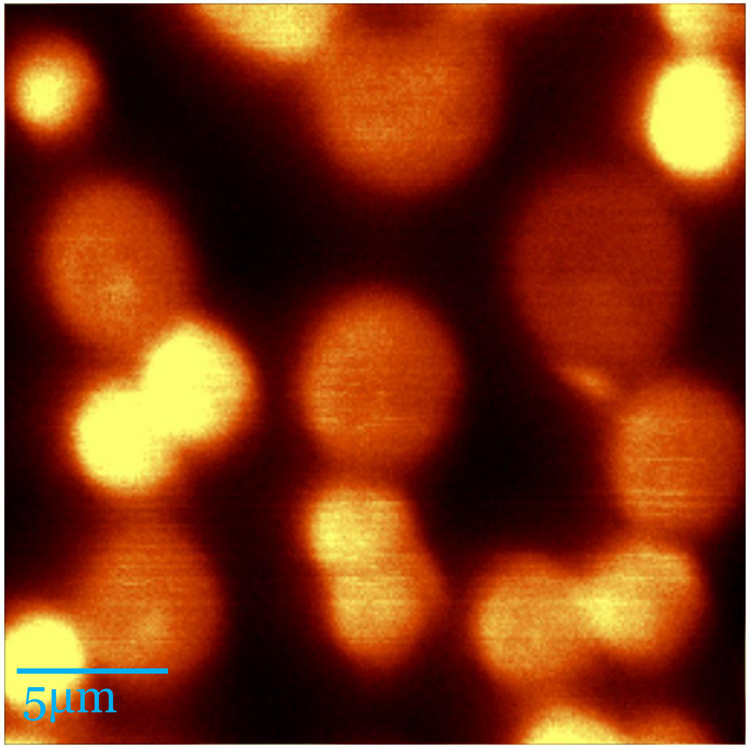
# Xray diffraction measurement

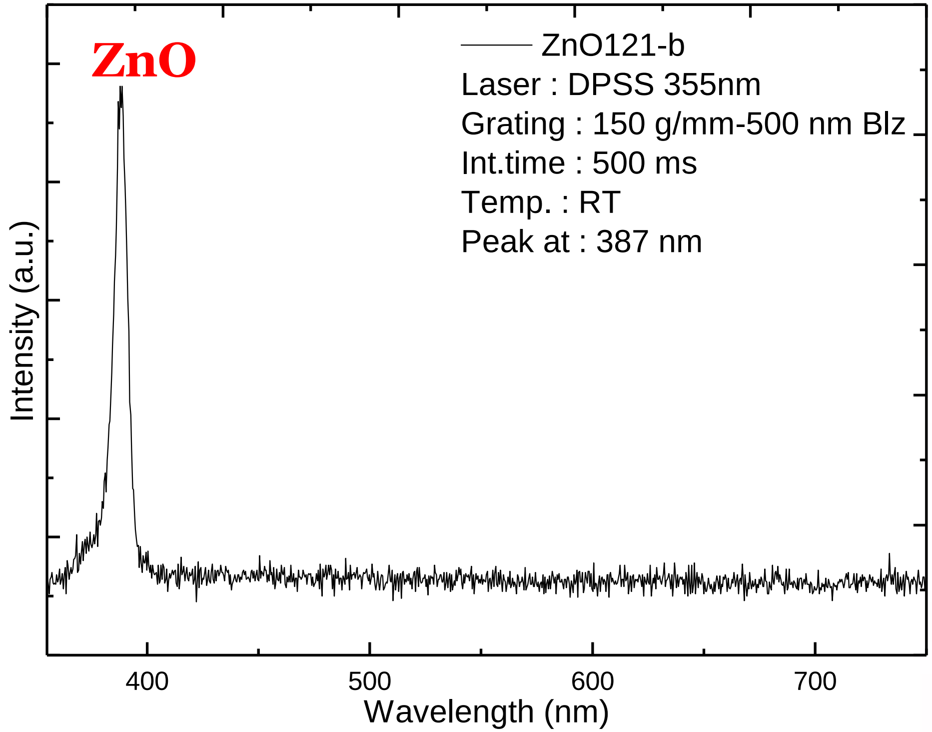


# Confocal PL of ZnO spheres

Confocal PL




No defects are observed

# Summary

- ✓ZnO polar surface was responsible for preferential growth
- ✓Structure directing agents (SDA) effectively passivated the ZnO polar surface, leading to balanced vertical and lateral growth rate
- ✓Careful combination of SDA allowed for the control of both size and size distribution of ZnO spheres

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- **Organic solar cells**
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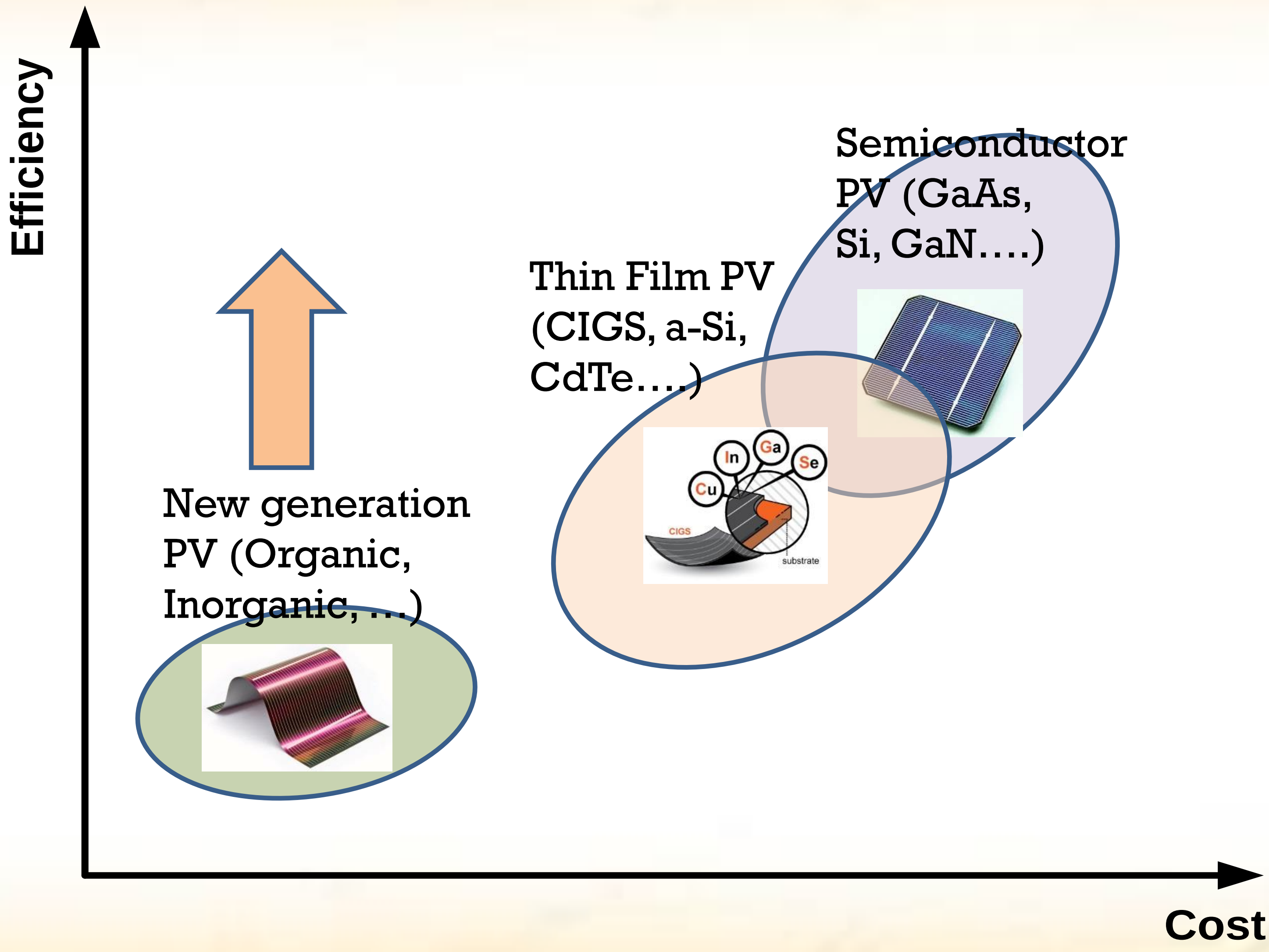
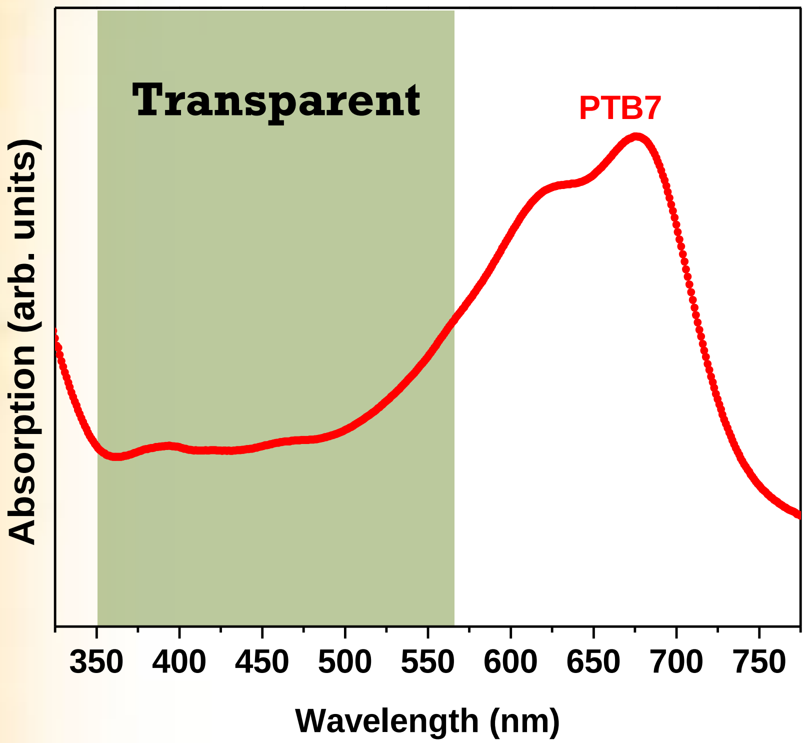
  - ✓ Degradation mechanisms of organic solar cells
  - ✓ Simulation of 3D organic morphologies
- **Power of His Words**

# Current state-of-the art solar cells

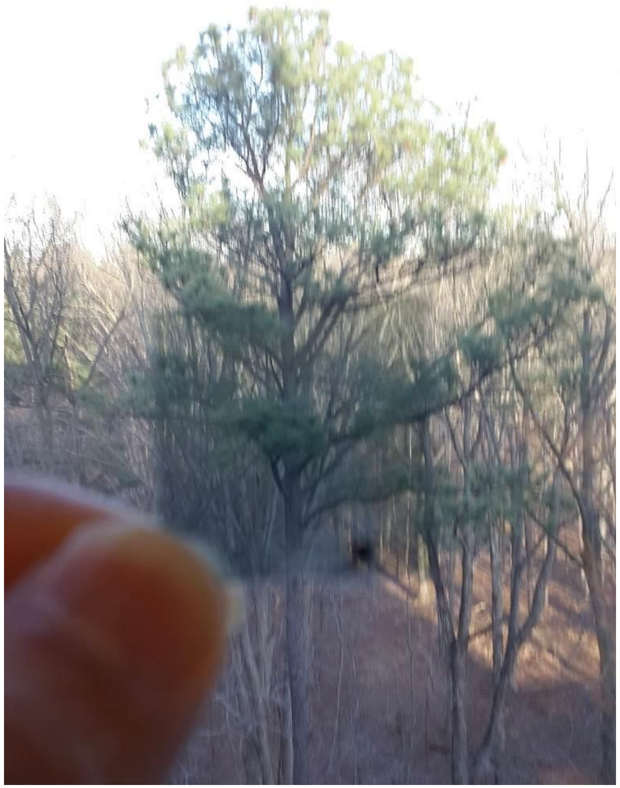


# Organic solar cells

**Absorption of polymer**

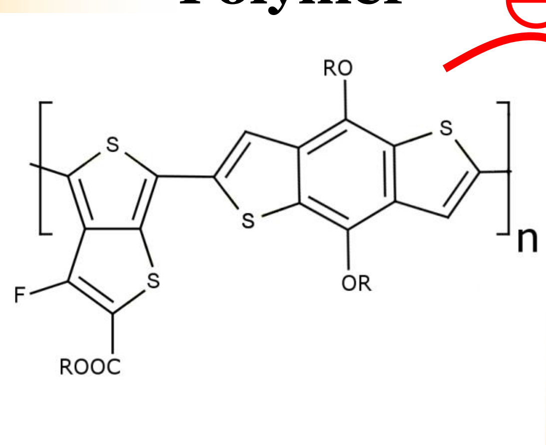



**Transparent solar cells**

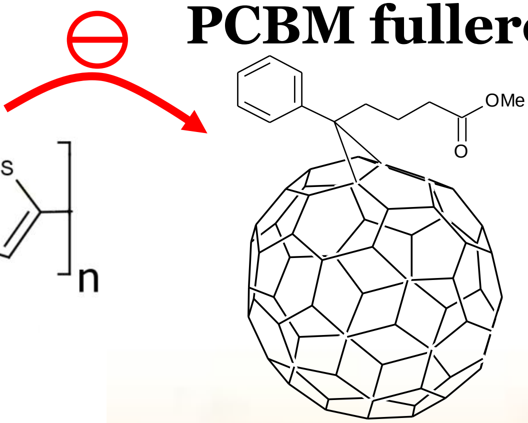


# Fabrication of organic solar cell

**Polymer** **PCBM fullerene**

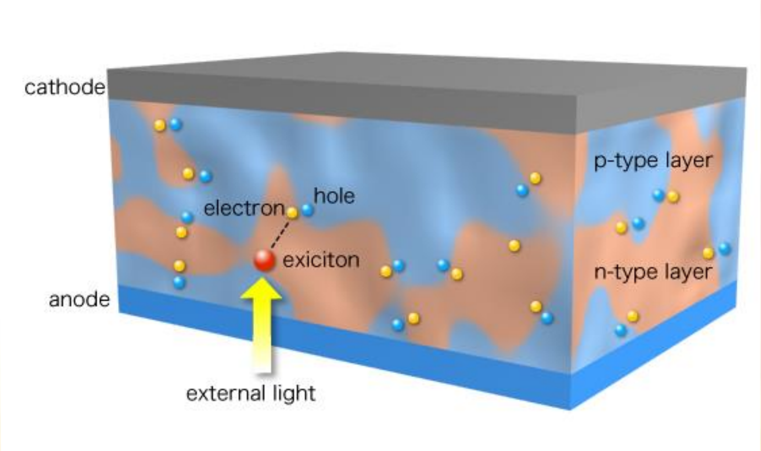



Donor

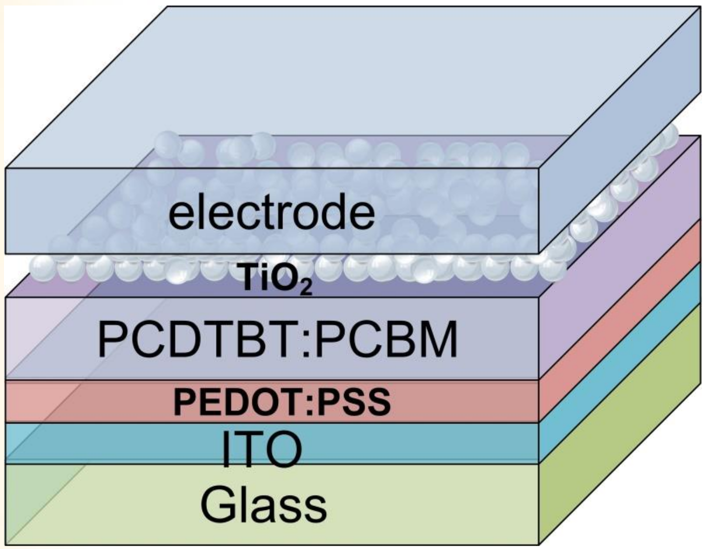


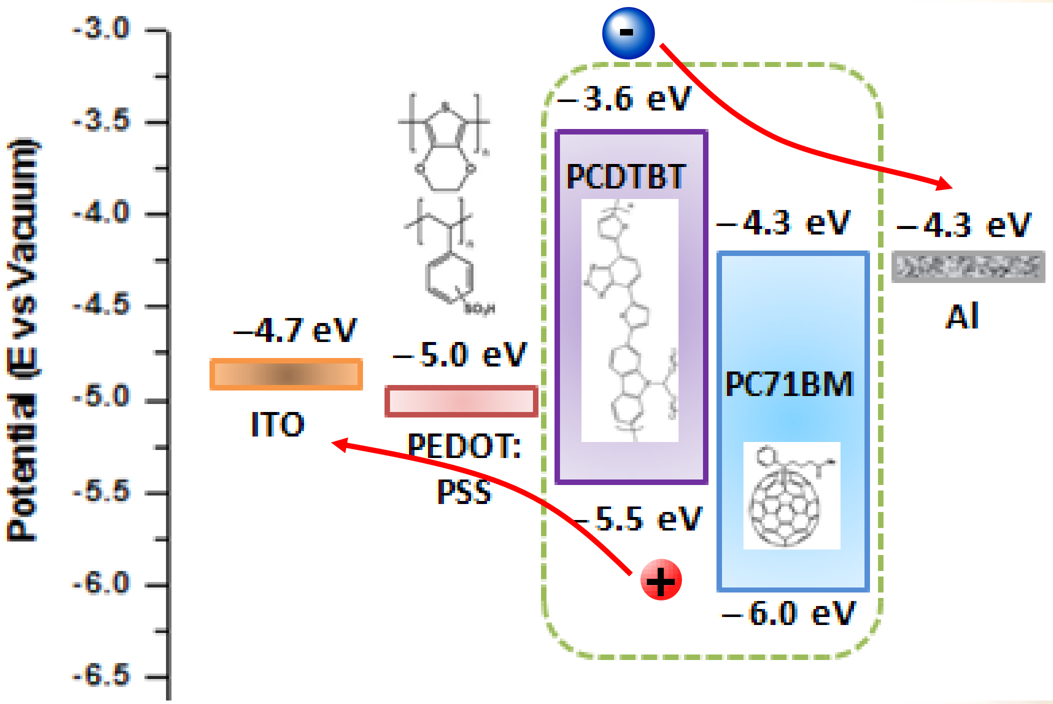

$PC_{71}BM$

Acceptor



# PCDTBT:PCBM solar cells

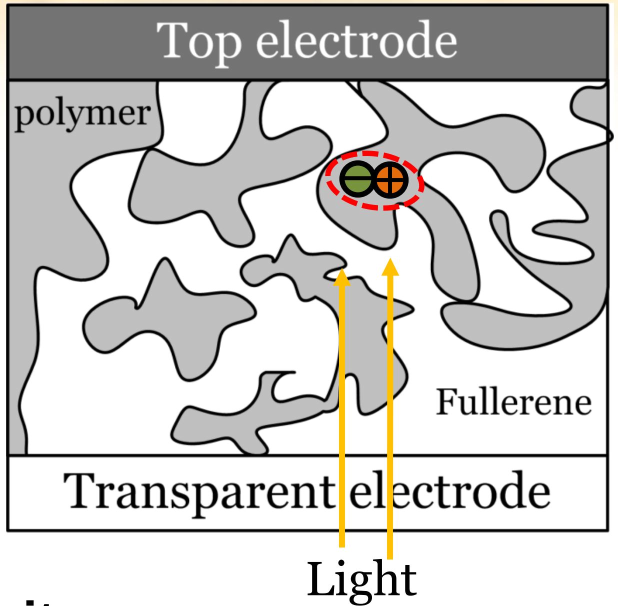


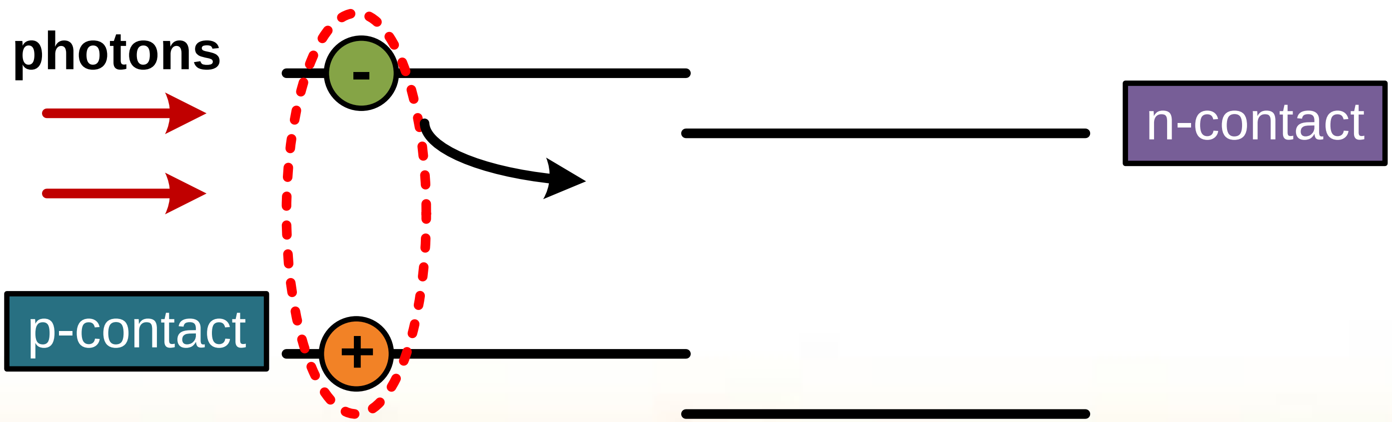




Heeger et al, Nature photonics, Vol 3, pp 297 (2009)

# Recombination processes

Exciton generation




$\tau_{exciton}$ =~ nanoseconds

# Recombination processes

**Heterojunction bipolar**

↓

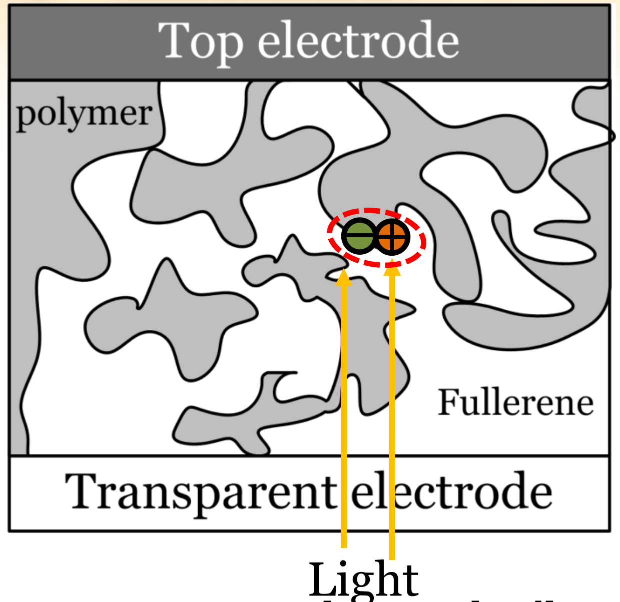
**Hetero-interface**

↓

**Dissociation center**

↓

**Nanoscale morphologies**

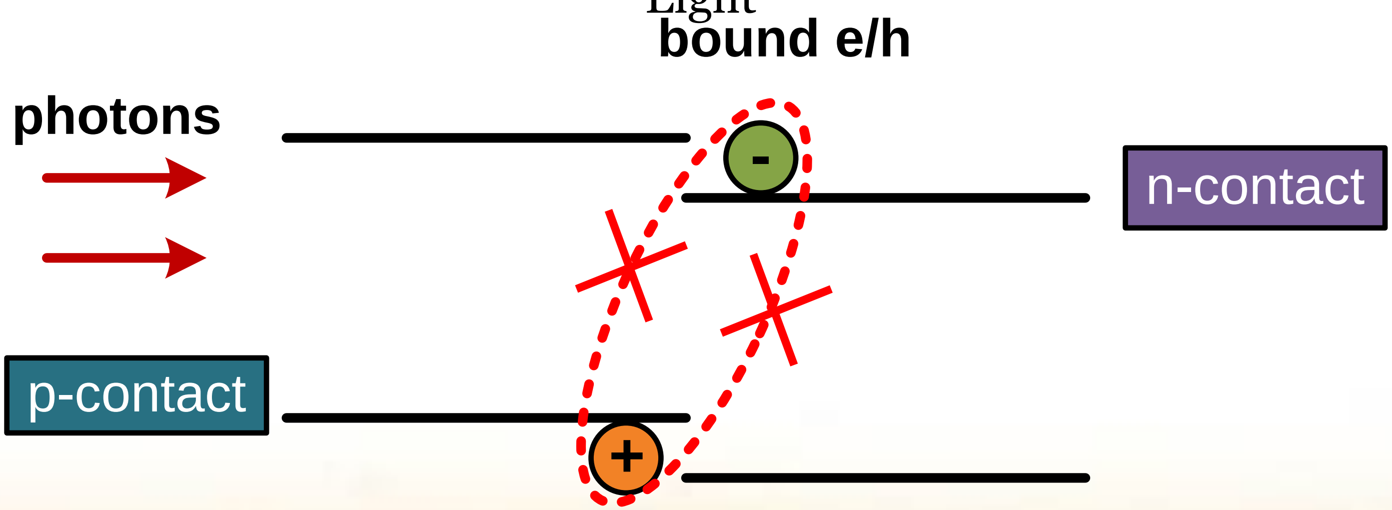



$\tau_{exciton}$=~10 ns

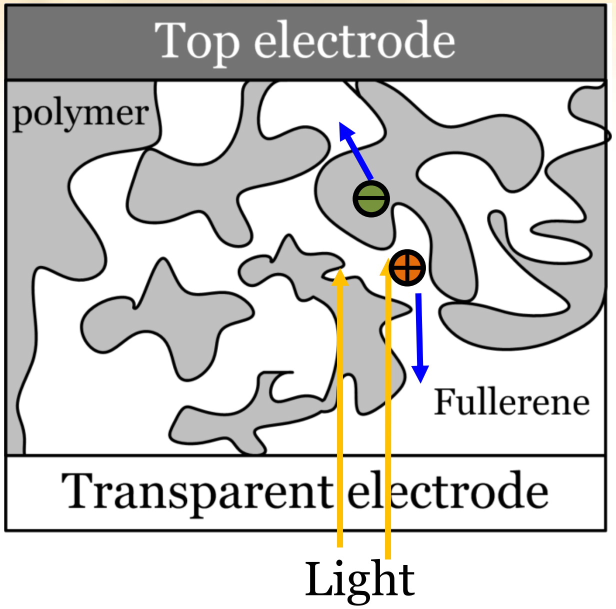
**Exciton diffusion length**

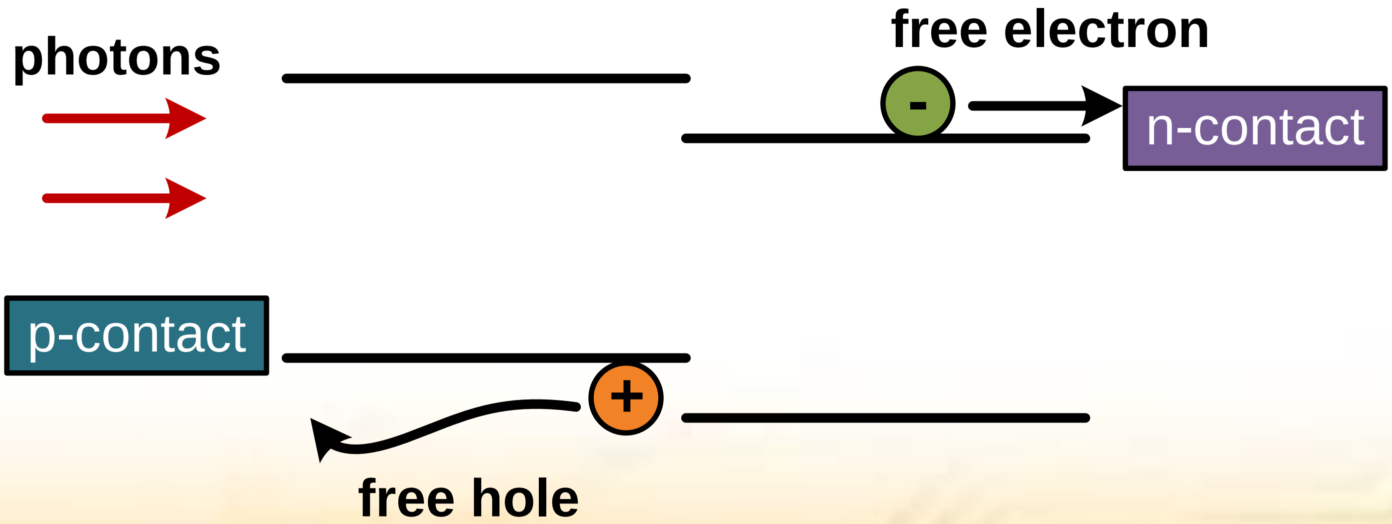
$$L_{exciton} = \sqrt{D\tau_{exciton}}$$

$$=\sim 10nm$$



# Recombination processes



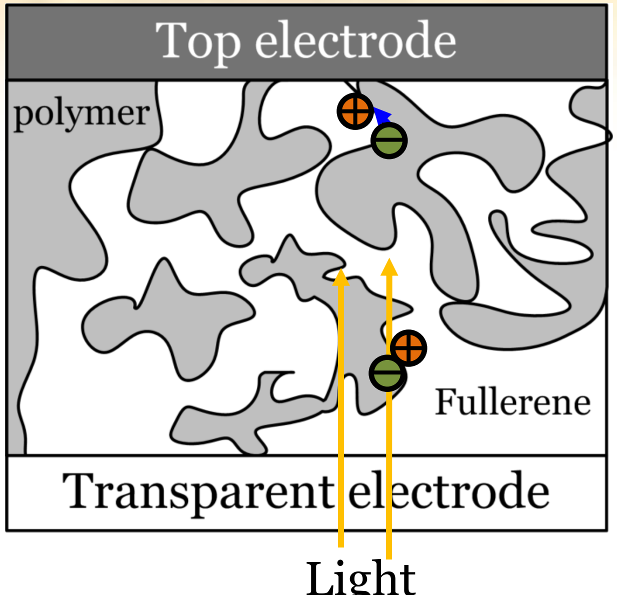



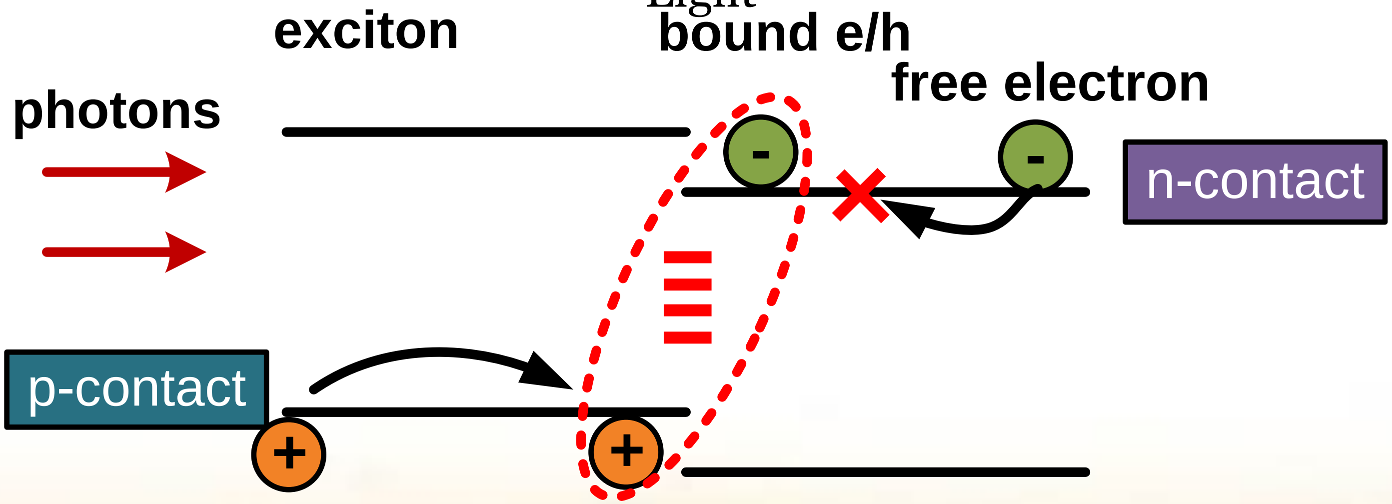
# Recombination processes

Langevin recombination

$$R = k_r(np - n_i^2)$$

$$k_r = \frac{q}{\varepsilon}(\mu_n + \mu_p)$$

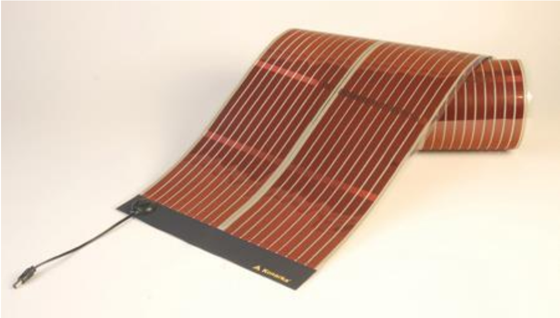



Namkoong et al, Organic electronics, Vol. 14, pp 74 (2013)

# Degradation of organic solar cells

Lifetime > 20 years



Lifetime < 6 years

# Degradation mechanisms of organic solar cells

Degradation processes of PPV(polyphenylene vinylene) polymer

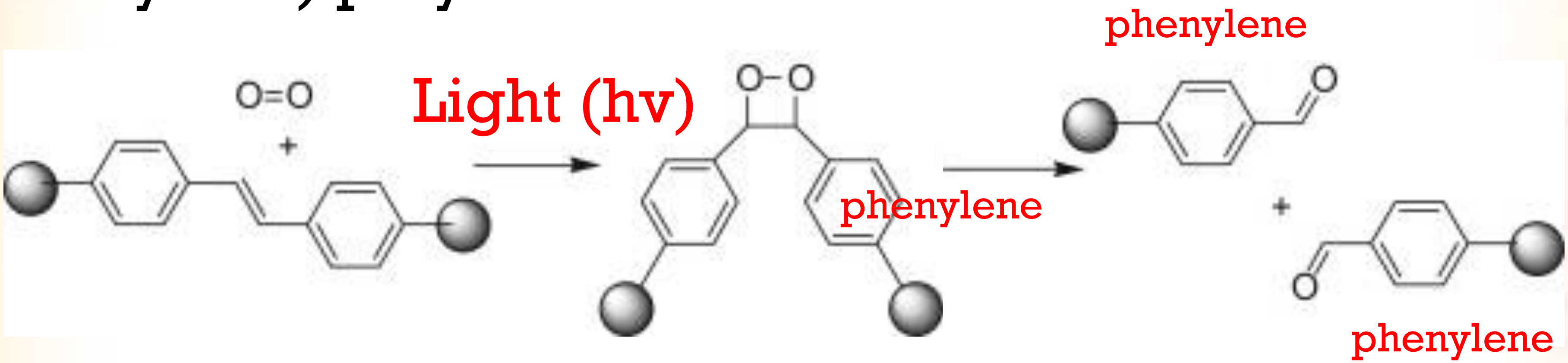
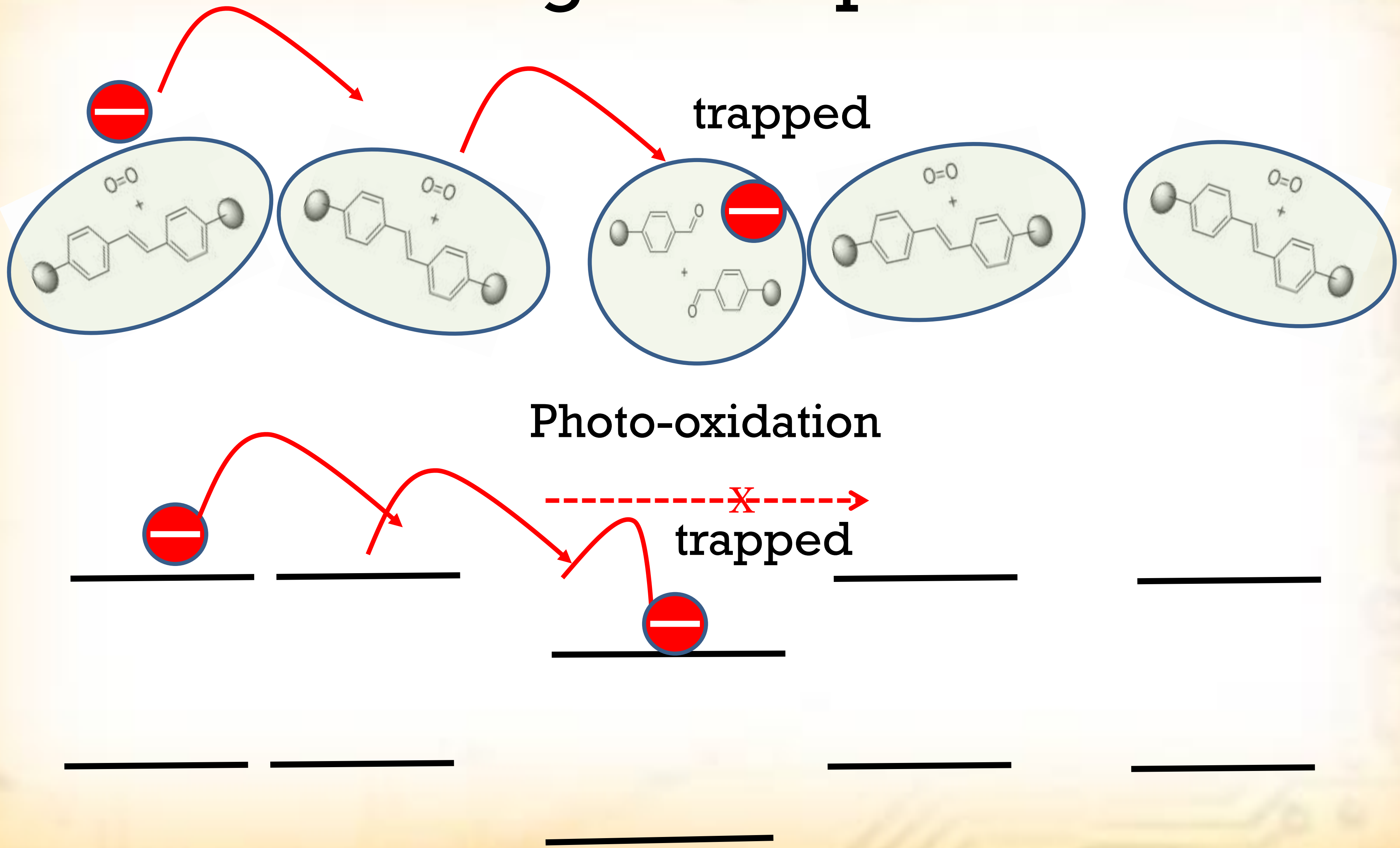



Photo-oxidation scission

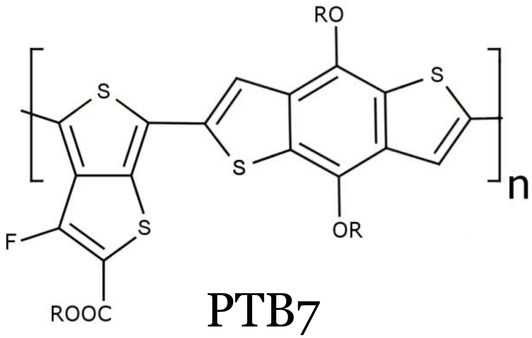
Reducing charge transport efficiency
Creating defects and trap centers

# Influence of photo-oxidation on charge transport



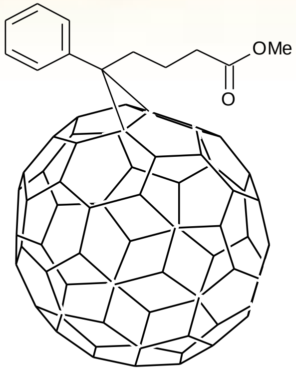
# Degradation of organic solar cells

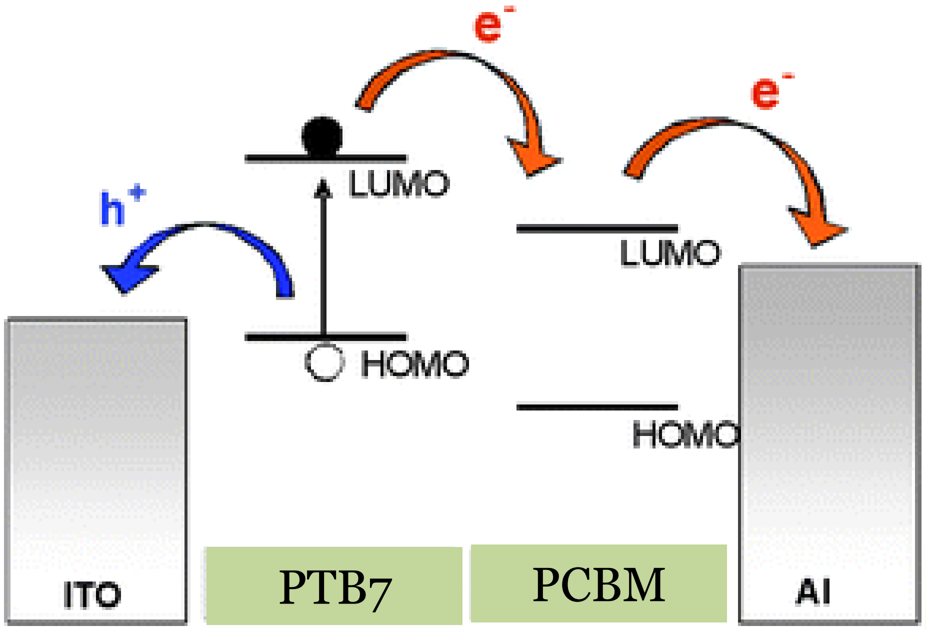
## Polymers




PTB7

## PCBM



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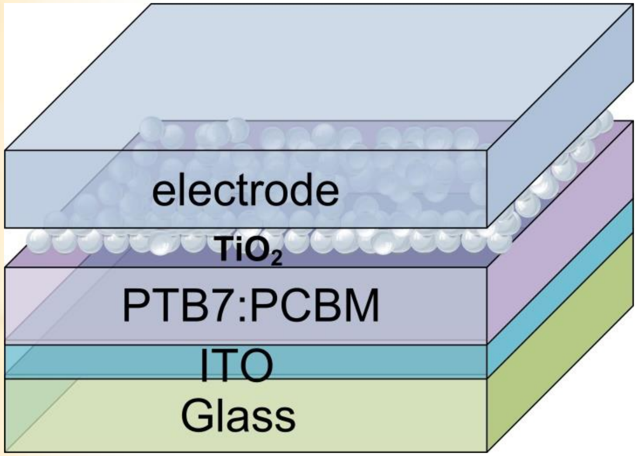
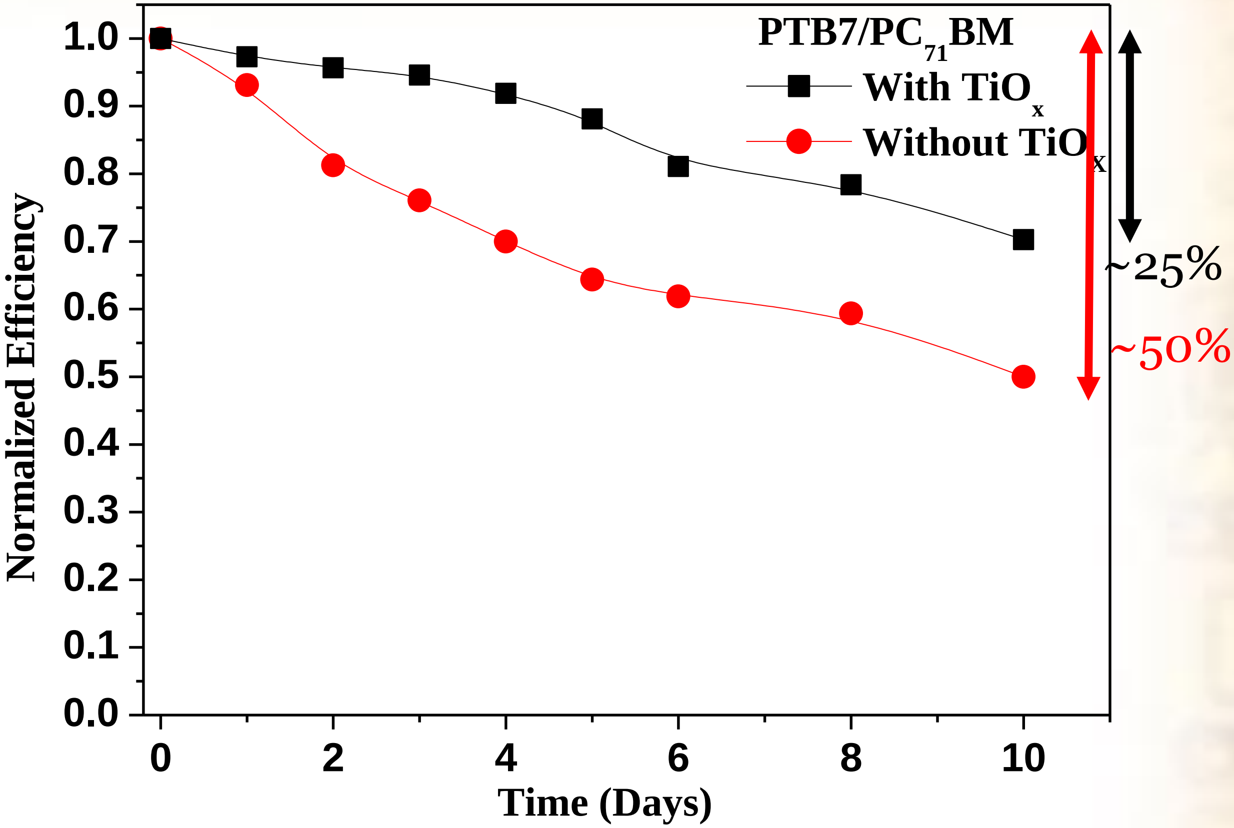
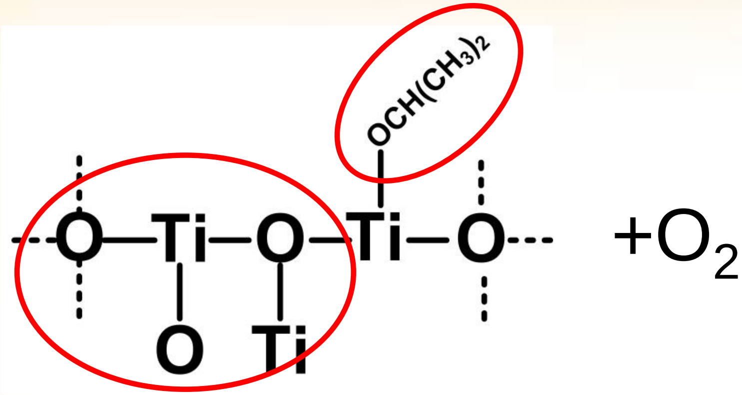
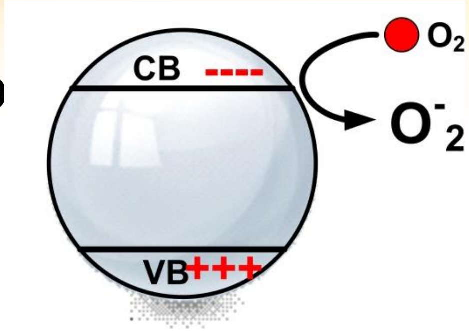


# Role of $TiO_2$ for organic solar cells

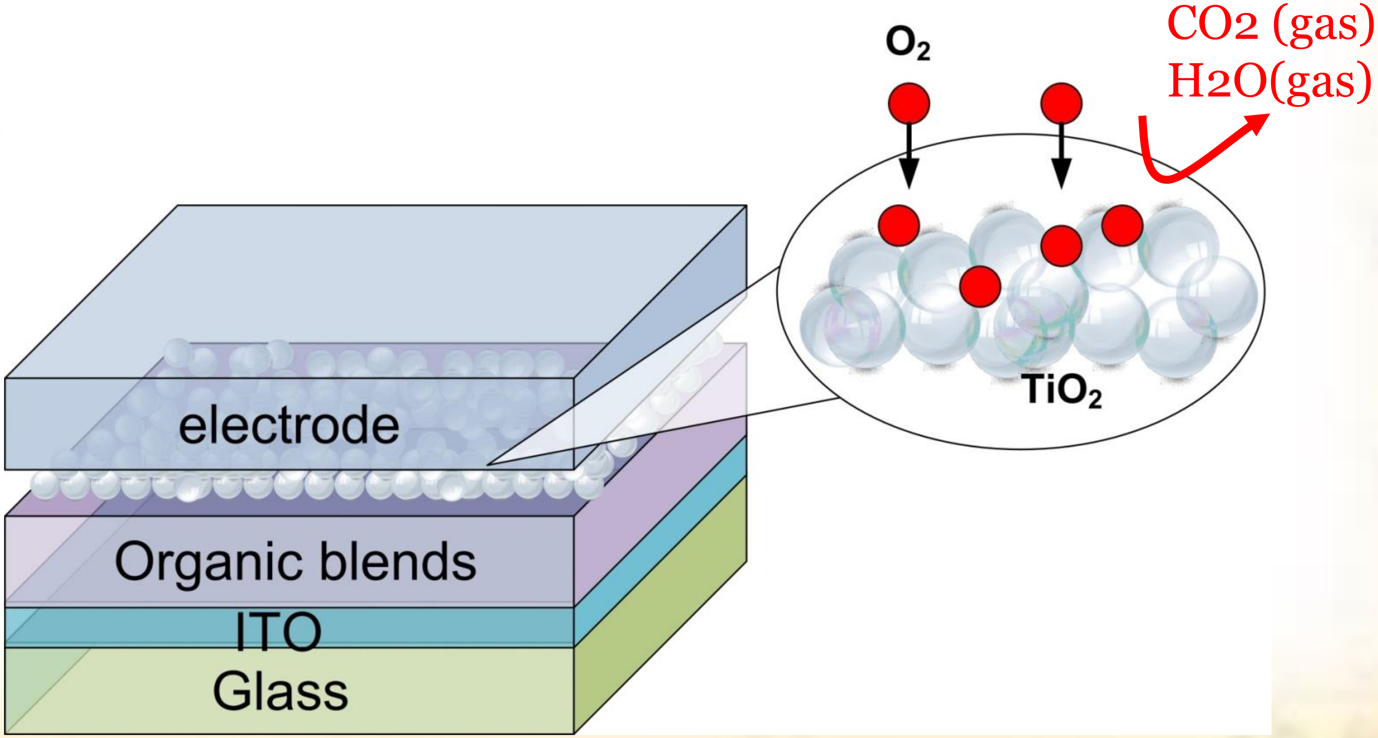



TiO

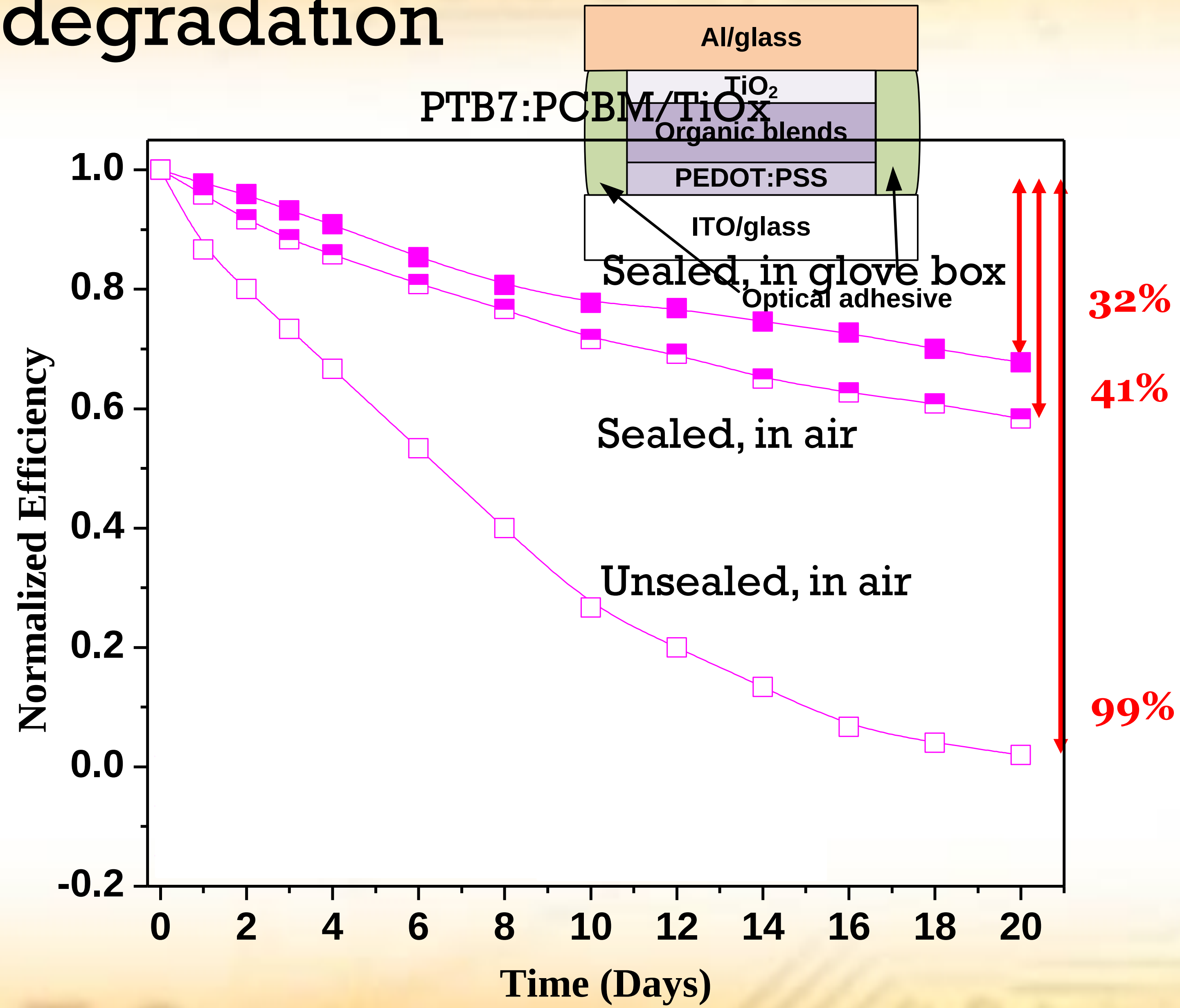



Redox process

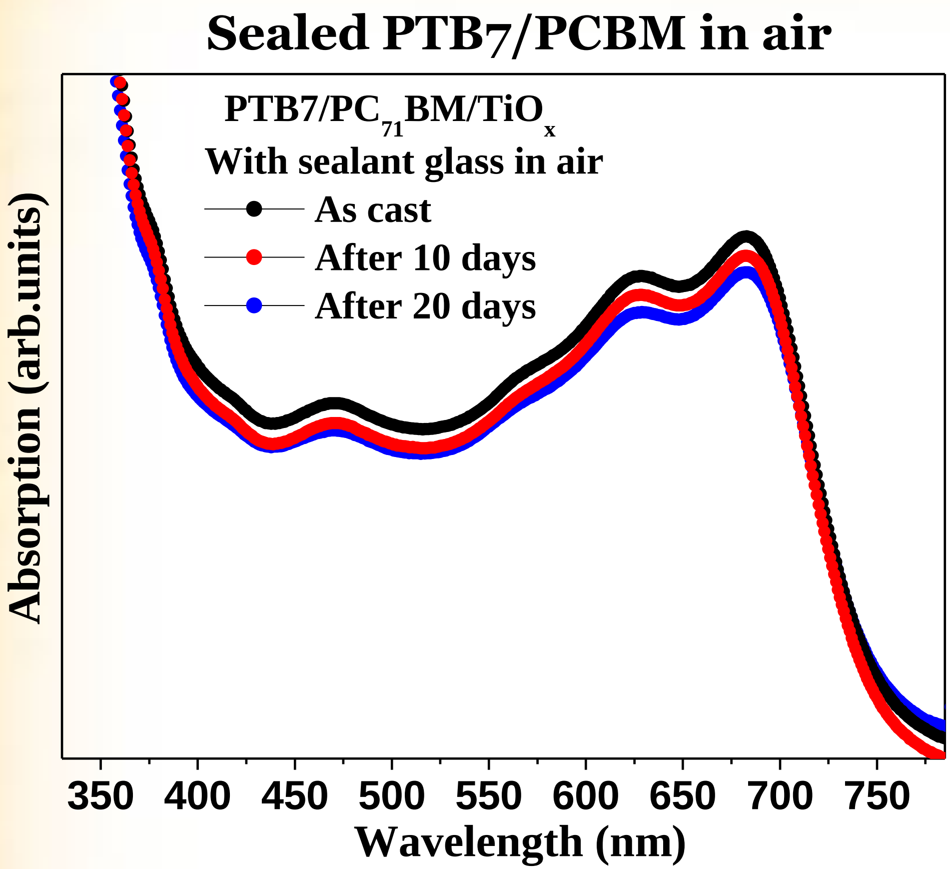
Sol-Gel processed $TiO_x$

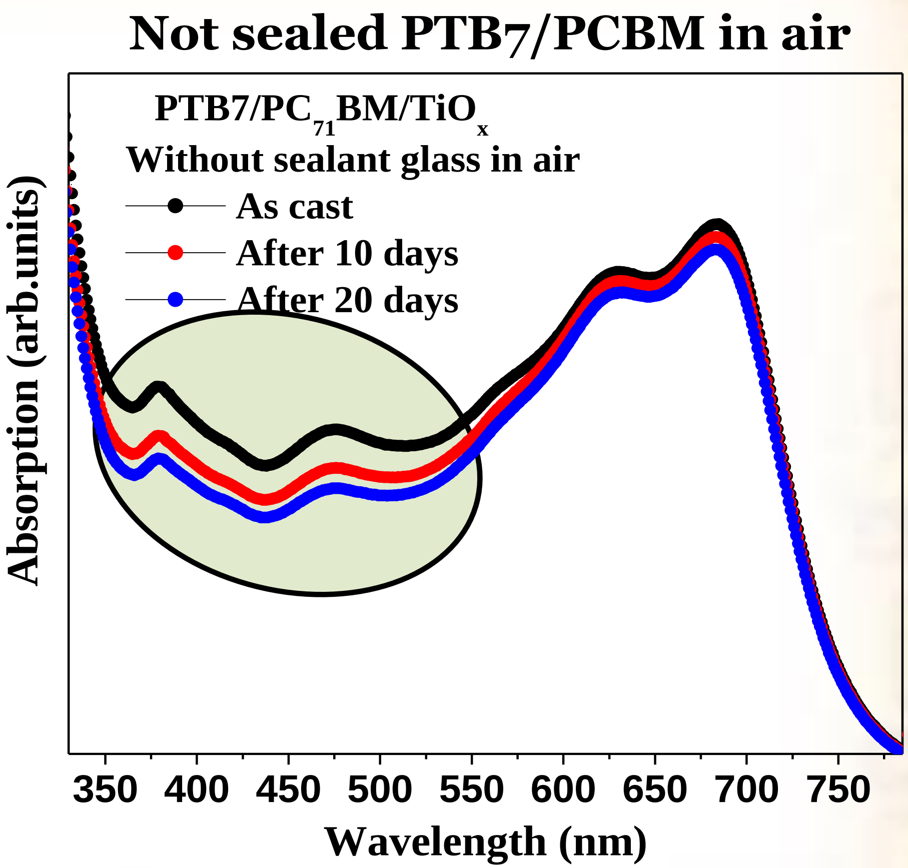


# Effect of sealing of organic solar cells on degradation

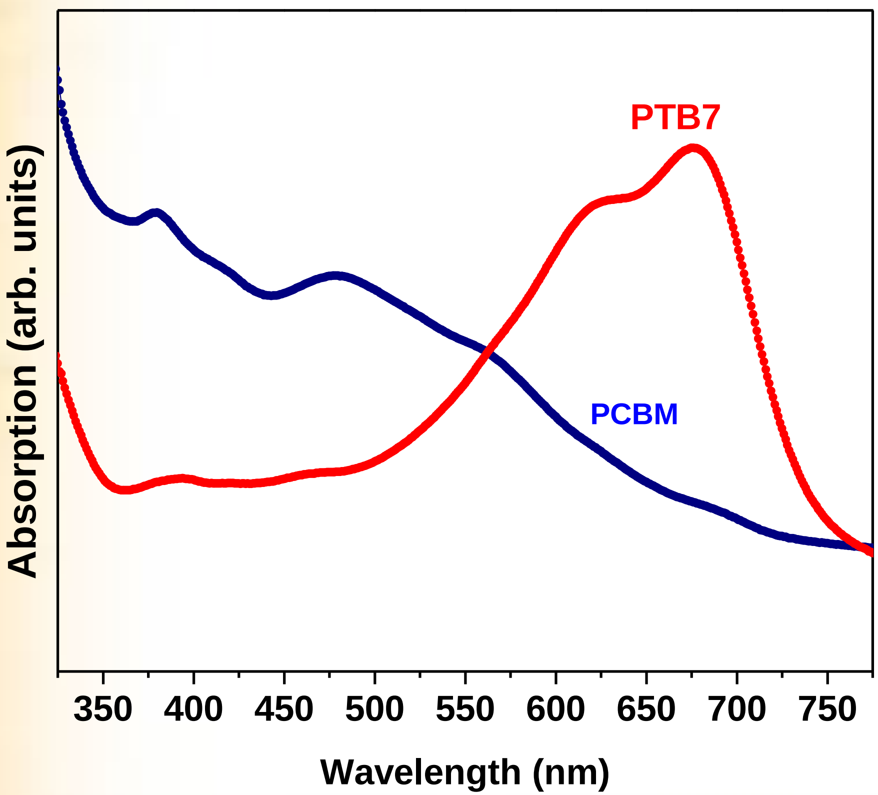


# Comparison of UV-VIS absorption

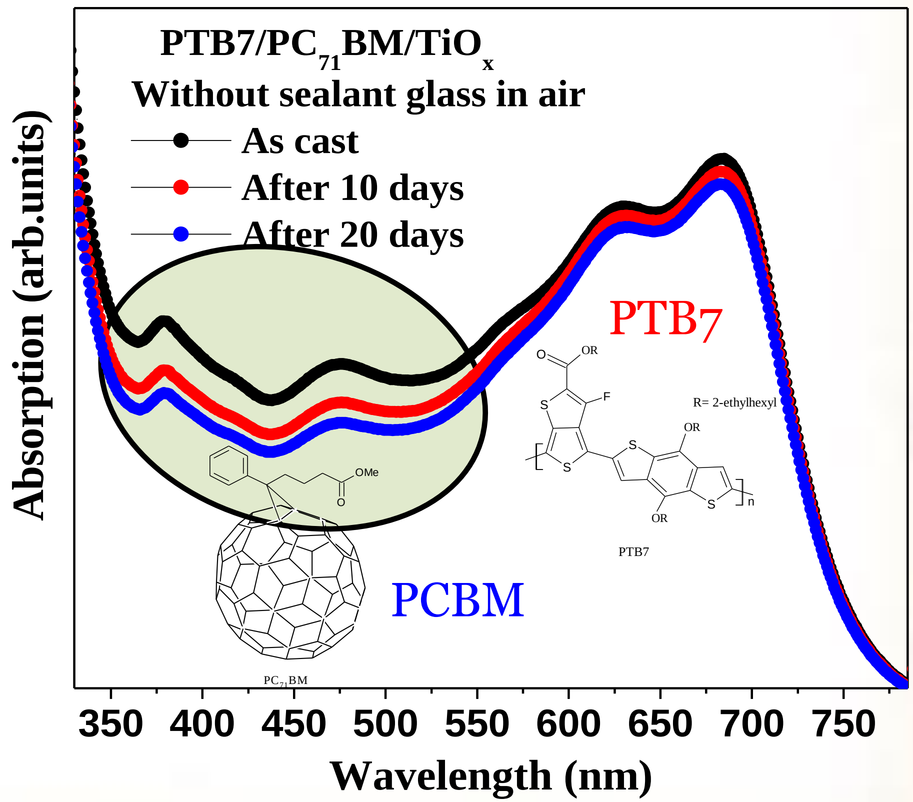


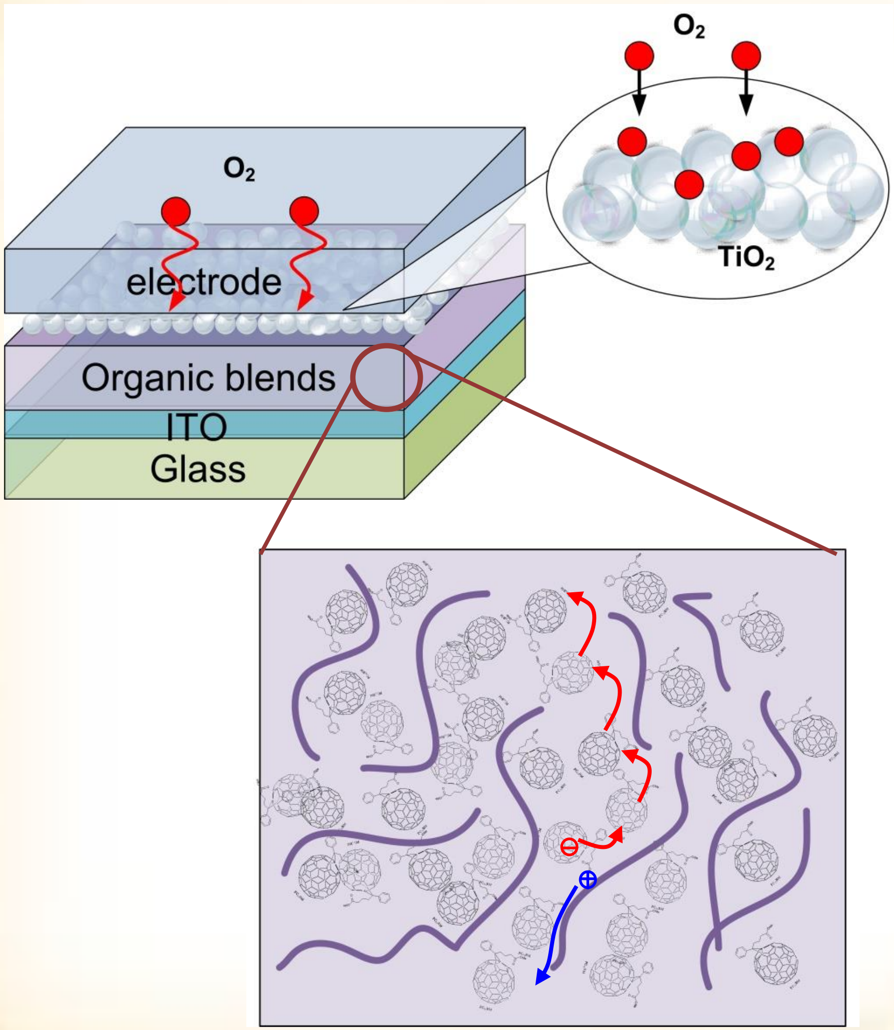
# Absorption of PTB7 and PCBM



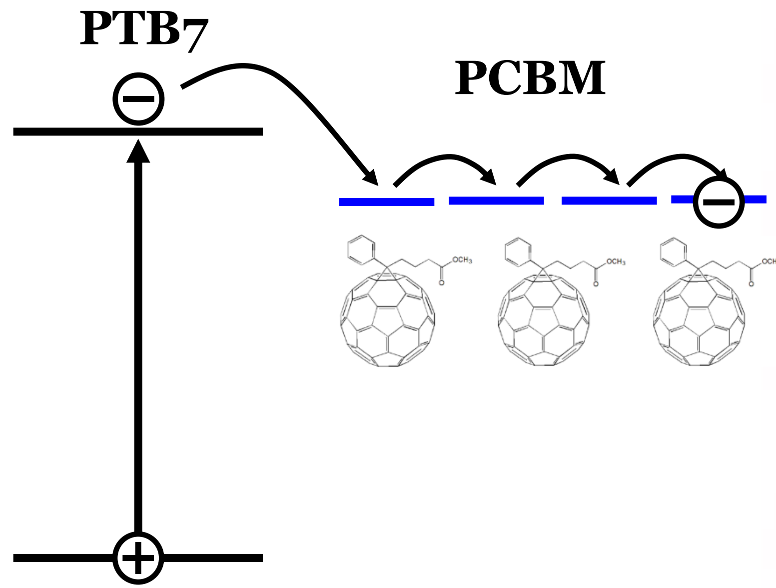

## Not sealed PTB7/PCBM in air



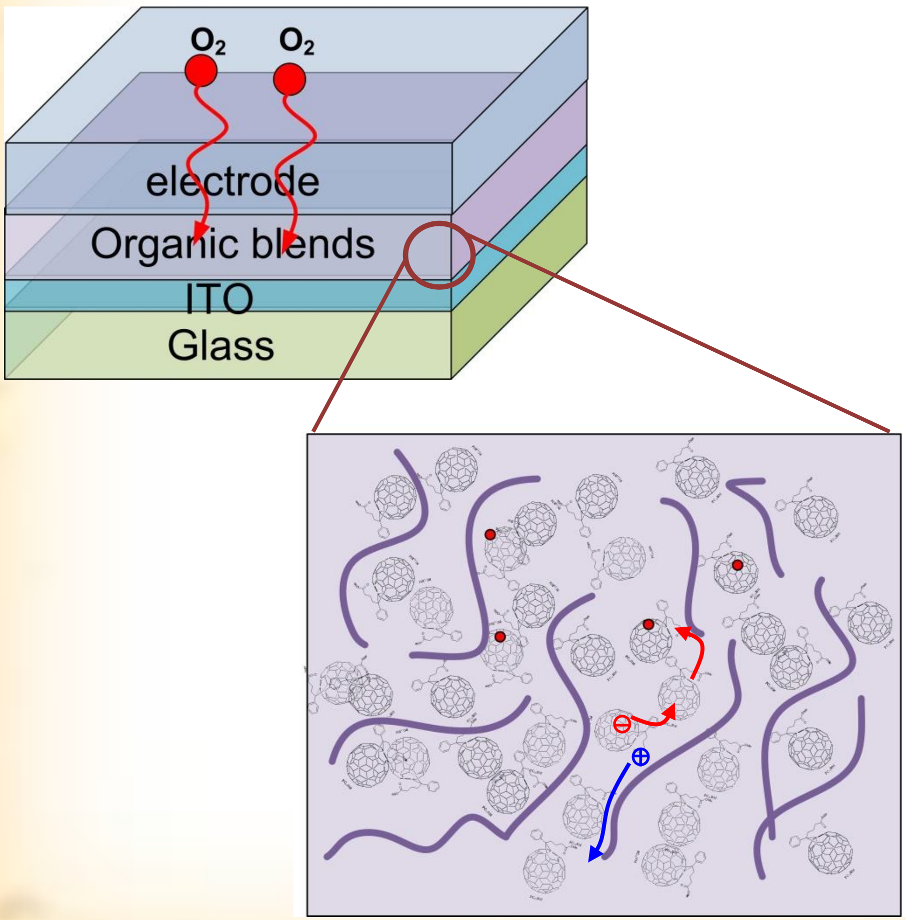
# Degradation mechanism for organic solar cells



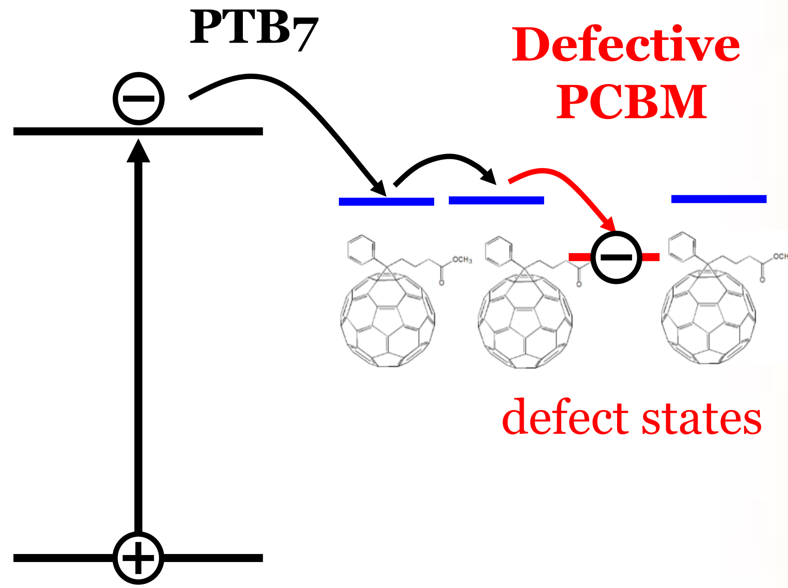

**Sealed PTB7/PCBM in air**



# Degradation mechanism for organic solar cells




**Not sealed PTB7/PCBM in air**




Namkoong et al, unpublished work (2014)

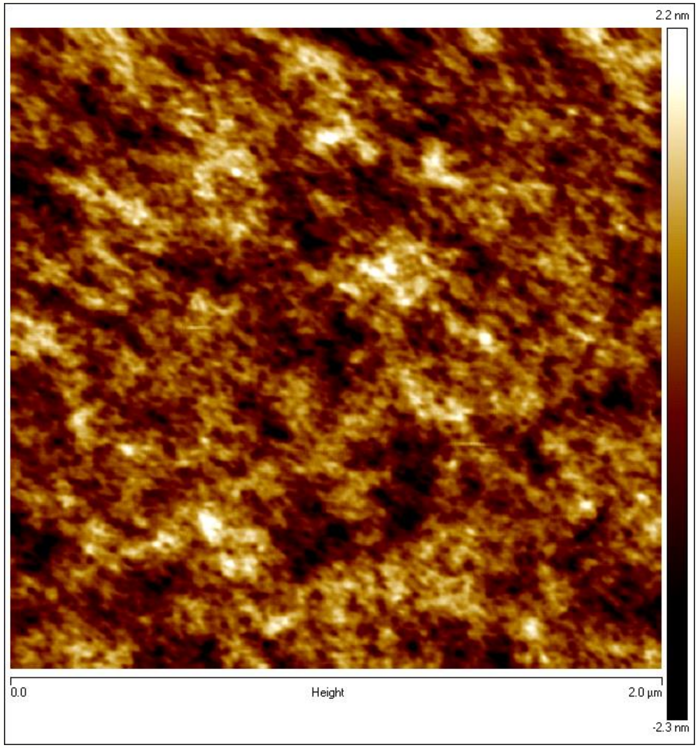
# Summary

- ✓ Degradation of organic solar cells is due to chemical degradation in the presence of oxygen
- ✓ Longer exposure to oxygen will create many defects and trap centers that will force organic solar cells to reduce lifetime
- ✓ The degradation of organic solar cells is governed by the degradation of PCBM rather than organic polymer

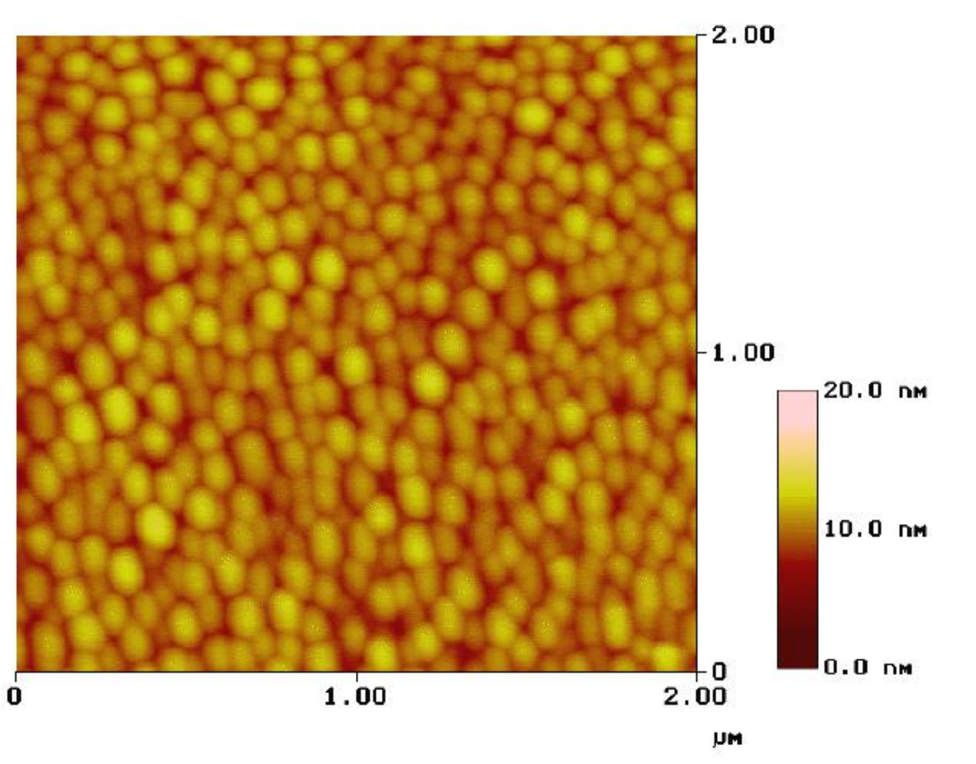
# Simulation of organic morphologies

# Simulation of organic morphologies

**AFM image of organic surface**



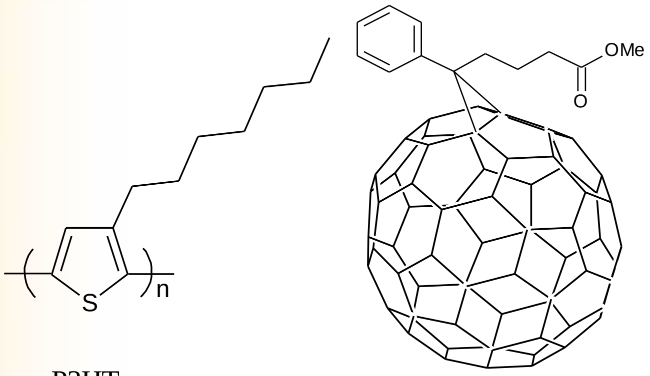

**Semiconductor surface**



# Simulation of organic morphologies

**Polymer: Fullerene**

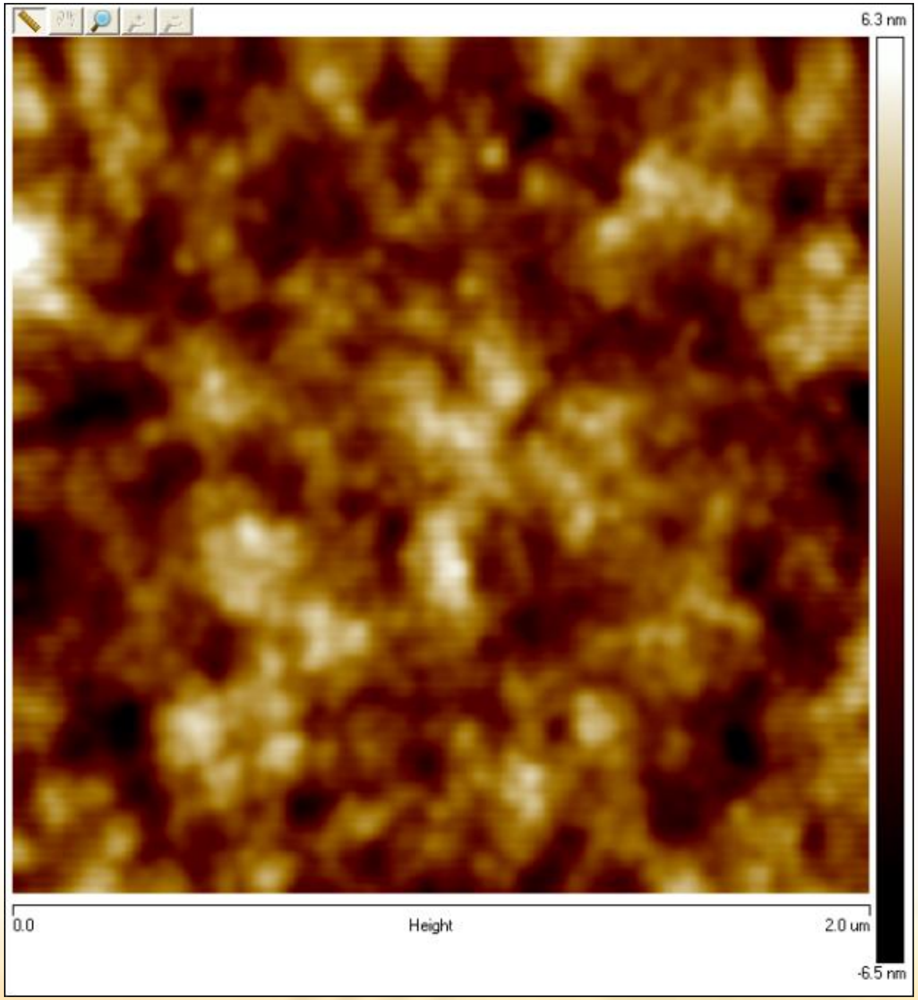
**1 : 1**




P3HT

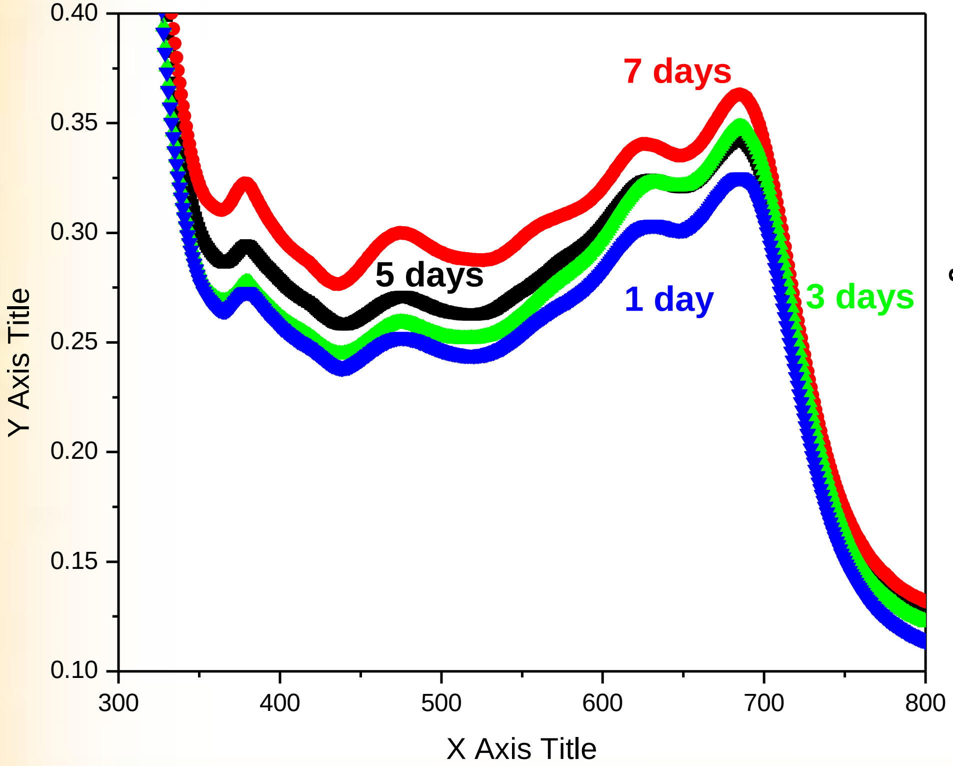
$PC_{71}BM$

7 days mixing

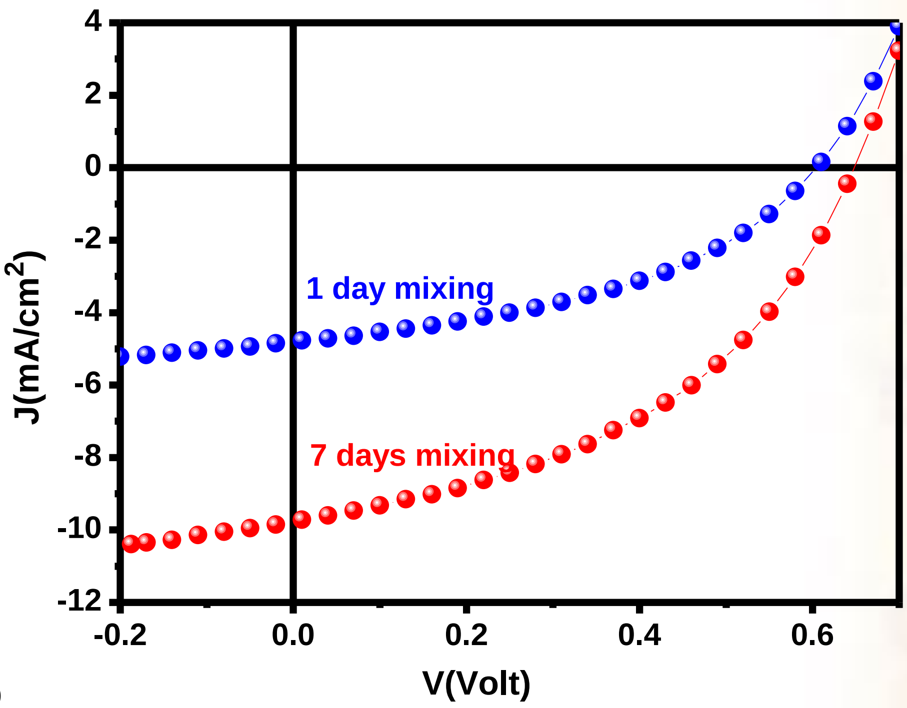


# Effect of uniform morphologes

## Light absorption

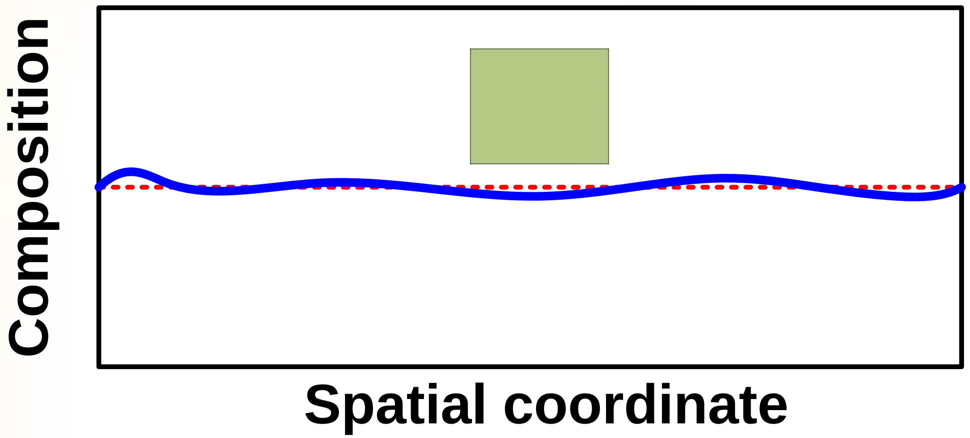


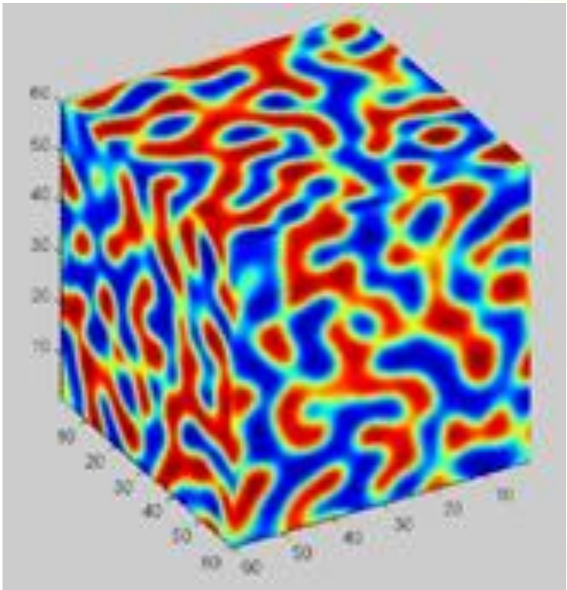

## JV characteristics



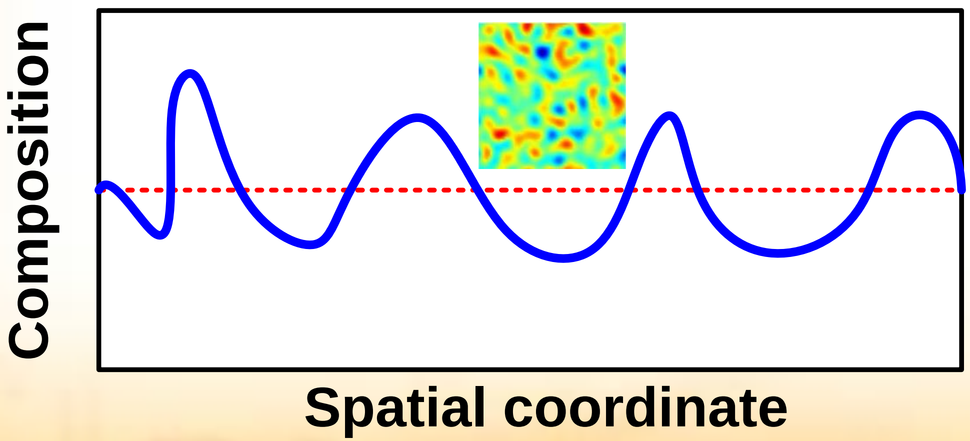
# Phase separation of organics

- Spinodal decomposition

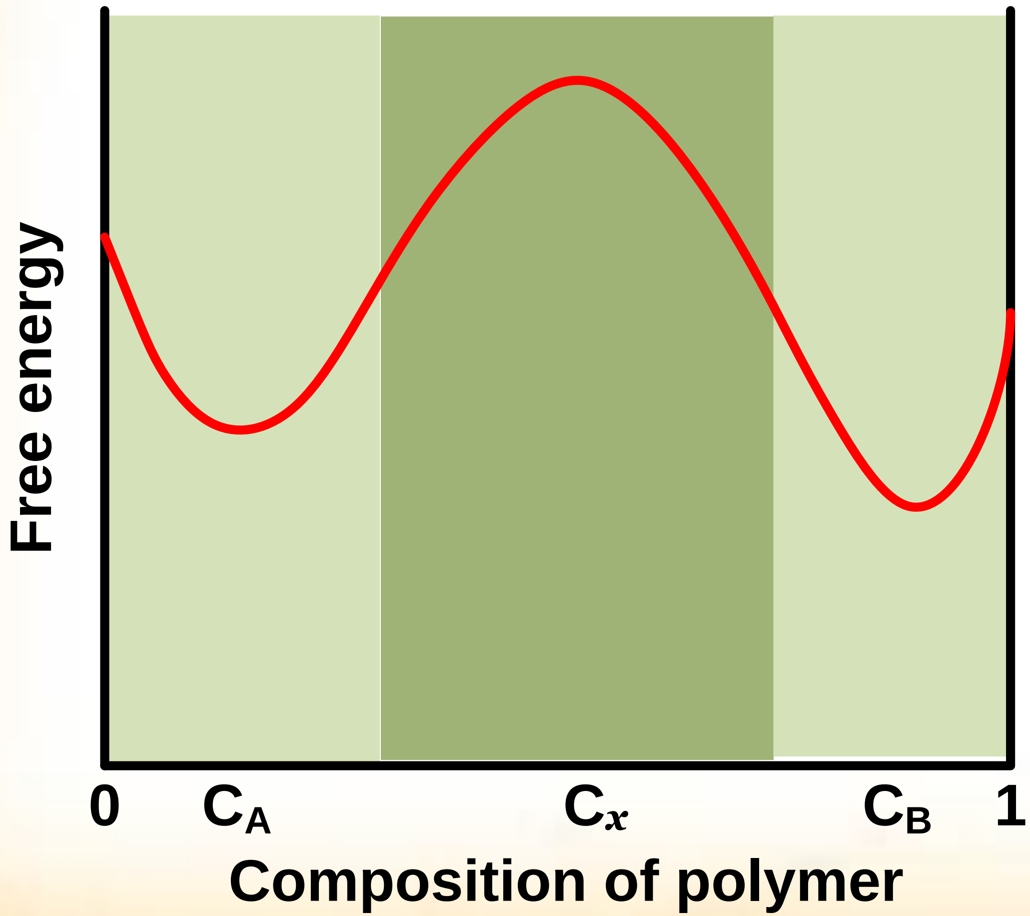


- Binodal decomposition



# Phase separation

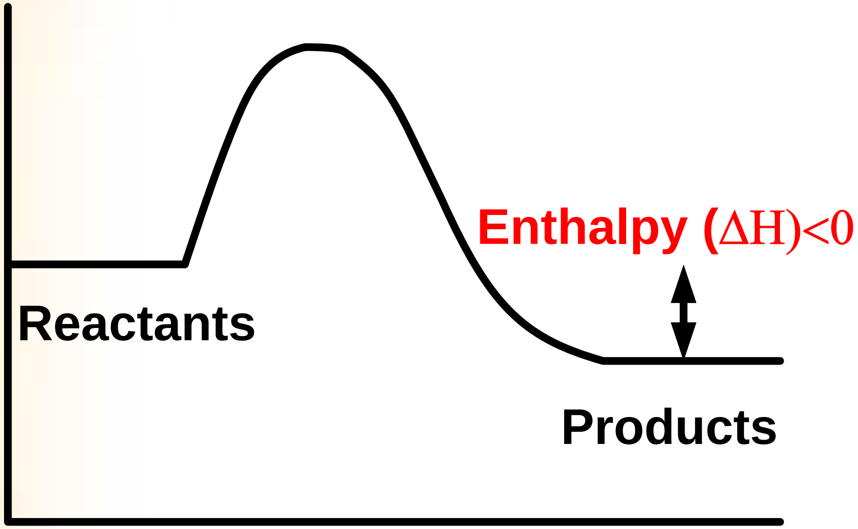



$$dG = dH - TdS$$

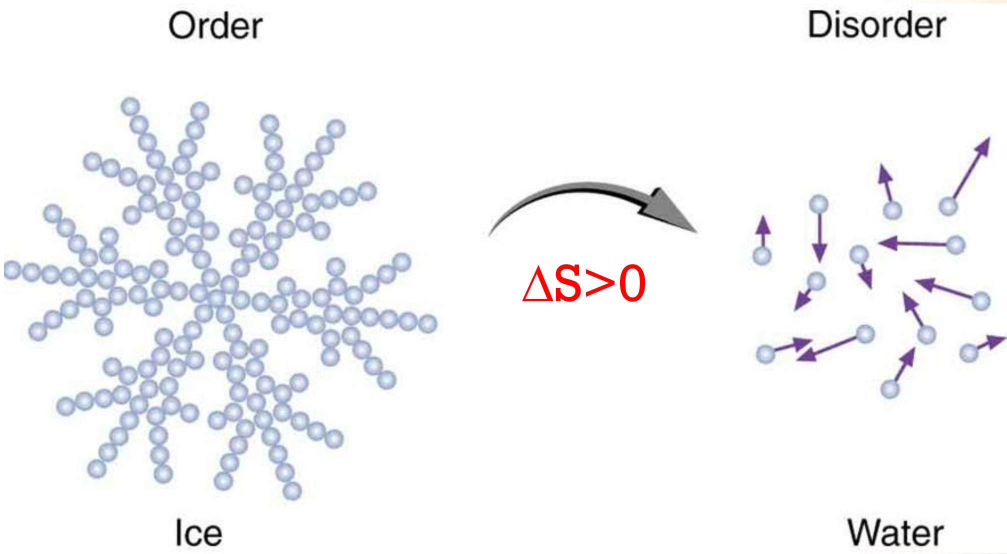
**G: Gibbs free energy**
**H: Enthalpy**
**S: Entropy**

# Spontaneous process

Enthalpy (H) defines system energy.

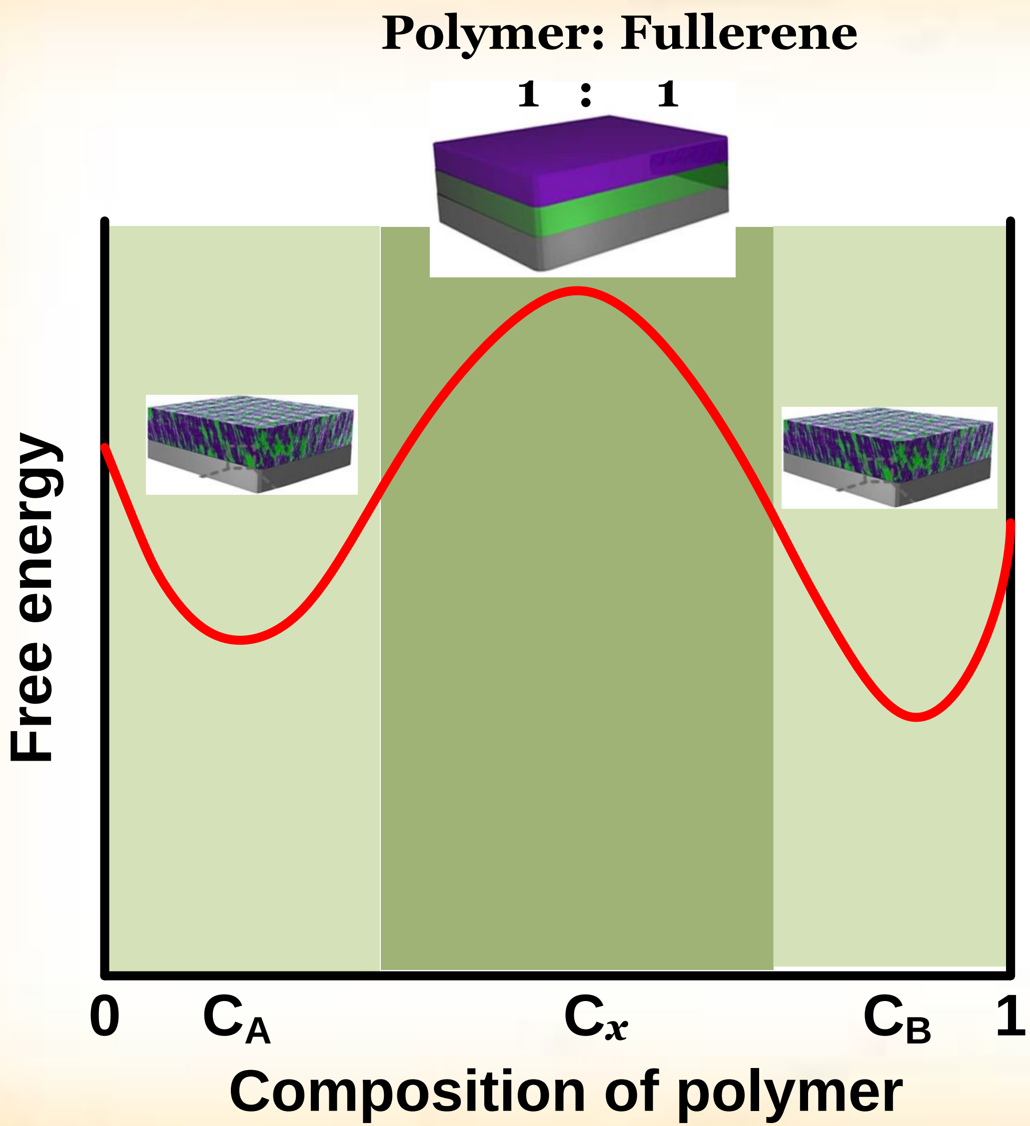



Entropy (S) measures disorders of systems




$$dG = dH - TdS < 0$$

# Phase separation



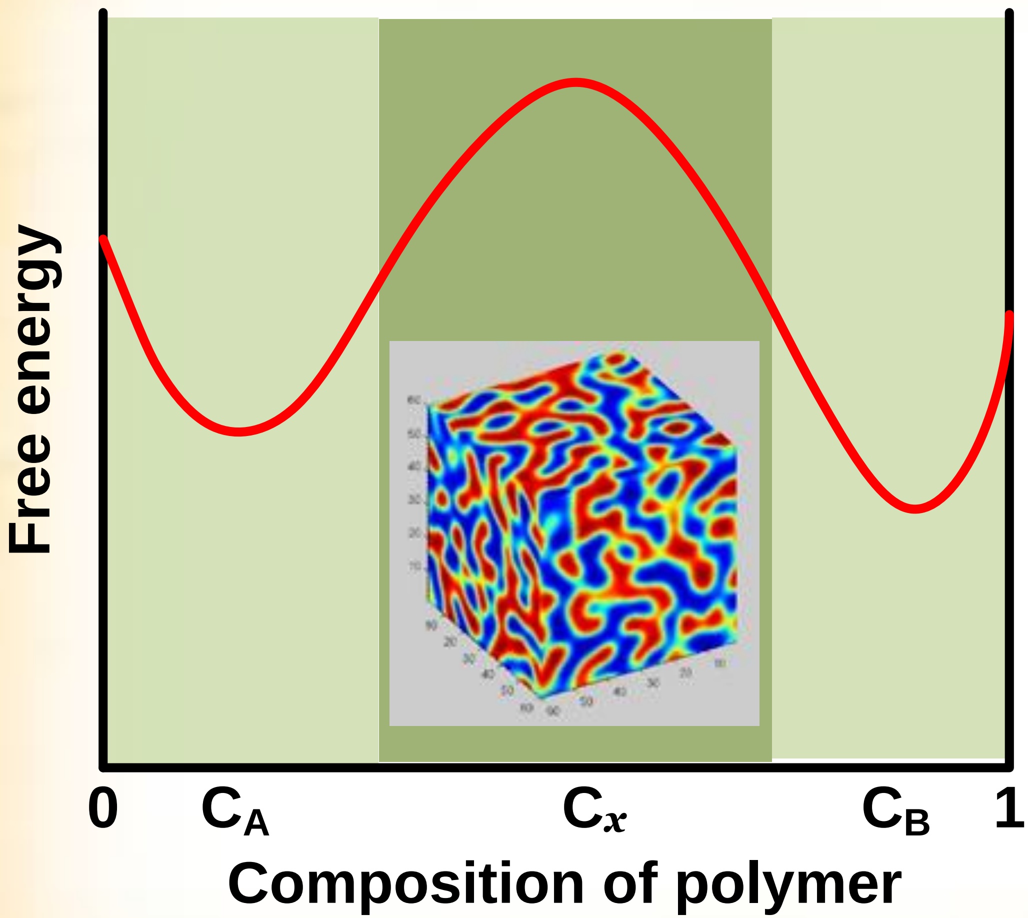

$$dG = dH - TdS$$

**G: Gibbs free energy**
**H: Enthalpy**
**S: Entropy** $dS>0$

$dG < 0$ **Spontaneous process**

$dG > 0$ **nonspontaneous process**

# Flory-Huggins/Allen-Cahn




Flory-Huggins type of free energy

$$f = \frac{RT}{v_{site}}\left(\frac{C_A}{m_A}\ln C_A + \frac{C_B}{m_B}\ln C_B + \chi_{AB}C_A C_B\right)$$

Allen-Cahn Equation

$$\frac{\partial C}{\partial t} = \nabla^2\left(M\frac{\partial f}{\partial C} - k^2\nabla^2 C\right)$$

C: concentration
a: solution parameter
M: diffusivity of the phase
*k*: gradient energy coefficient

# Numerical simulation of partial differential equations

- Finite different method

$$\frac{\partial f}{\partial t} = \frac{\partial^2 f}{\partial x^2}$$

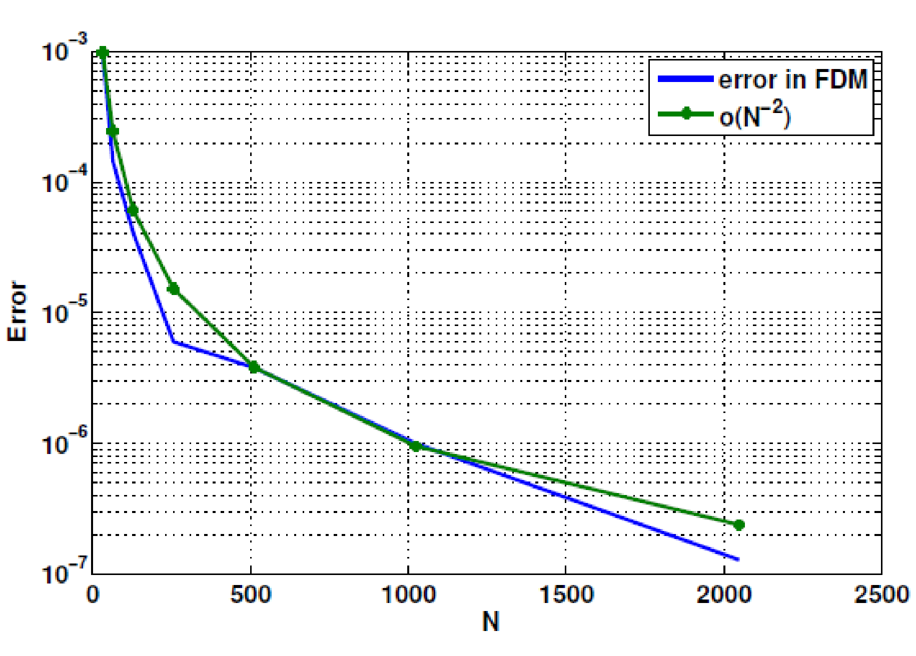
$$\frac{\partial^2 f}{\partial x^2} \approx \frac{f_{i-1} - 2f_i + f_{i+1}}{\Delta^2} + O(\Delta^2)$$

Not suitable for higher order differential equation
⇒Memory issues
⇒Large truncated errors
⇒Convergence issues

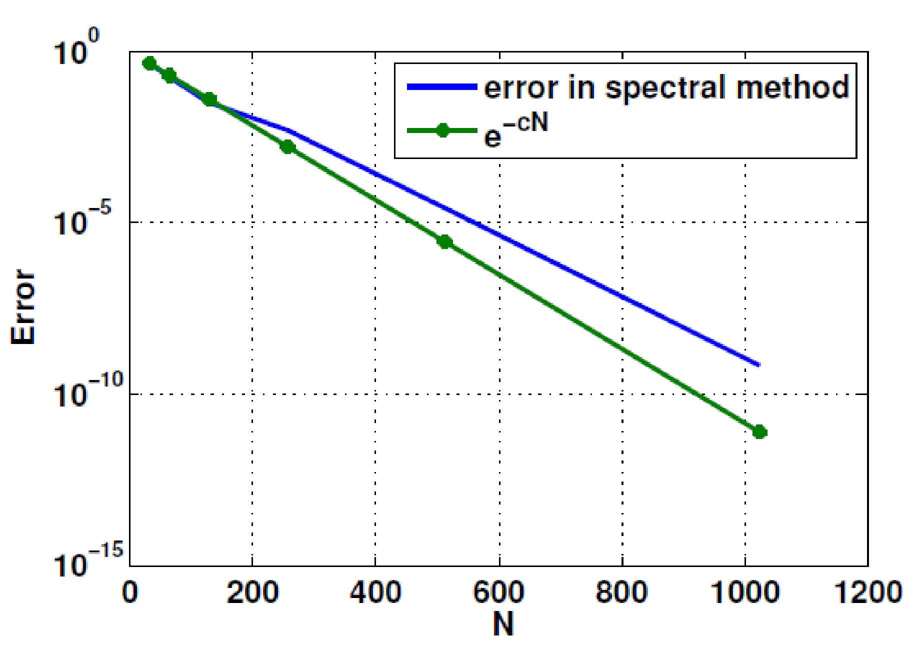
$$\begin{pmatrix} b_1 & a_1 & & & & \\ c_2 & b_2 & a_2 & & & \\ & c_3 & b_3 & a_3 & & \\ & & & & & \\ & & & c_{n-1} & b_{n-1} & c_{n-1} \\ & & & & c_n & b_n \end{pmatrix} \begin{pmatrix} f_1 \\ f_2 \\ f_3 \\ \\ f_{n-1} \\ f_n \end{pmatrix} = \begin{pmatrix} f_1'' \\ f_2'' \\ f_3'' \\ \\ f_{n-1}'' \\ f_n'' \end{pmatrix}$$

# Finite different vs. Spectral method

## Finite different method




## Spectral method



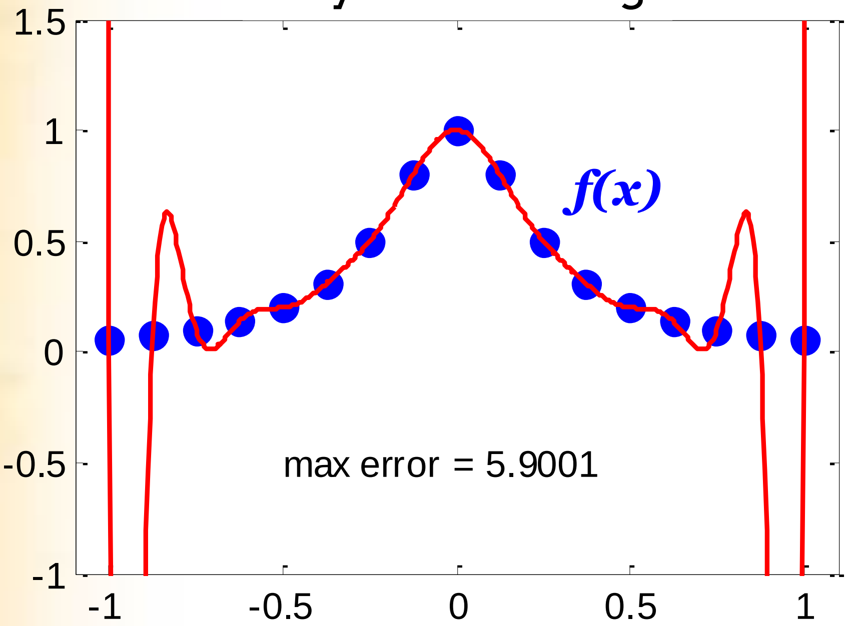

M. Mehra *et al*, Comparison between different numerical methods for discretization of PDEs.

# Spectral methods

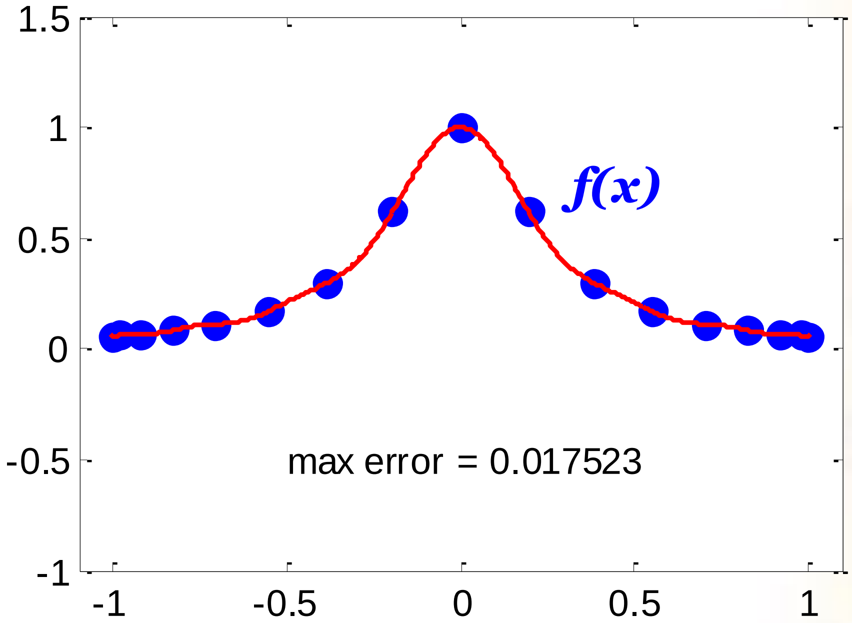
$$f(x) \approx \sum_{k=0}^{N} a_k \Phi_k(x)$$

$\phi$: interpolating function

Polynomial fitting




Trigonometric fitting




$\Phi_k(x)$ *polynomials*

$\Phi_k(x) = e^{ikx}$ *Fourier spectral method*

$$e^{ikx} = \cos(kx) + i\sin(kx)$$

# 1D Allen-Cahn equation

$$\frac{\partial u}{\partial t} = \varepsilon \frac{\partial^2 u}{\partial x} + u - u^3$$

$$FFT(u_j) \equiv \hat{u}_k$$

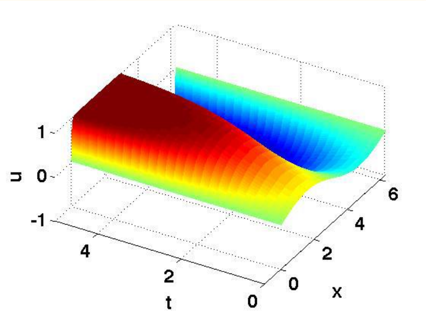
$$\frac{\partial \hat{u}_k}{\partial t} = \varepsilon (ik)^2 \hat{u}_k + \hat{u}_k - \hat{u}_k^3$$

$$\frac{\hat{u}_k^{n+1} - \hat{u}_k^{n}}{h} = \varepsilon (ik)^2 \hat{u}_k^{n+1} + \hat{u}_k^{n} - \widehat{(u^n)}_k^3$$

$$\hat{u}_k^{n+1} = \frac{\hat{u}_k^{n}(1/h + 1) - \widehat{(u^n)}_k^3}{(-\varepsilon (ik)^2 + 1/h)}$$

Inverse FFT

$$u = iFFT(\hat{u})$$



# 3D Allen-Cahn Equations

Flory-Huggins type of free energy

$$f = \frac{RT}{v_{site}} \left( \frac{C_A}{m_A} \ln C_A + \frac{C_B}{m_B} \ln C_B + \chi_{AB} C_A C_B \right)$$

Allen-Cahn Equation

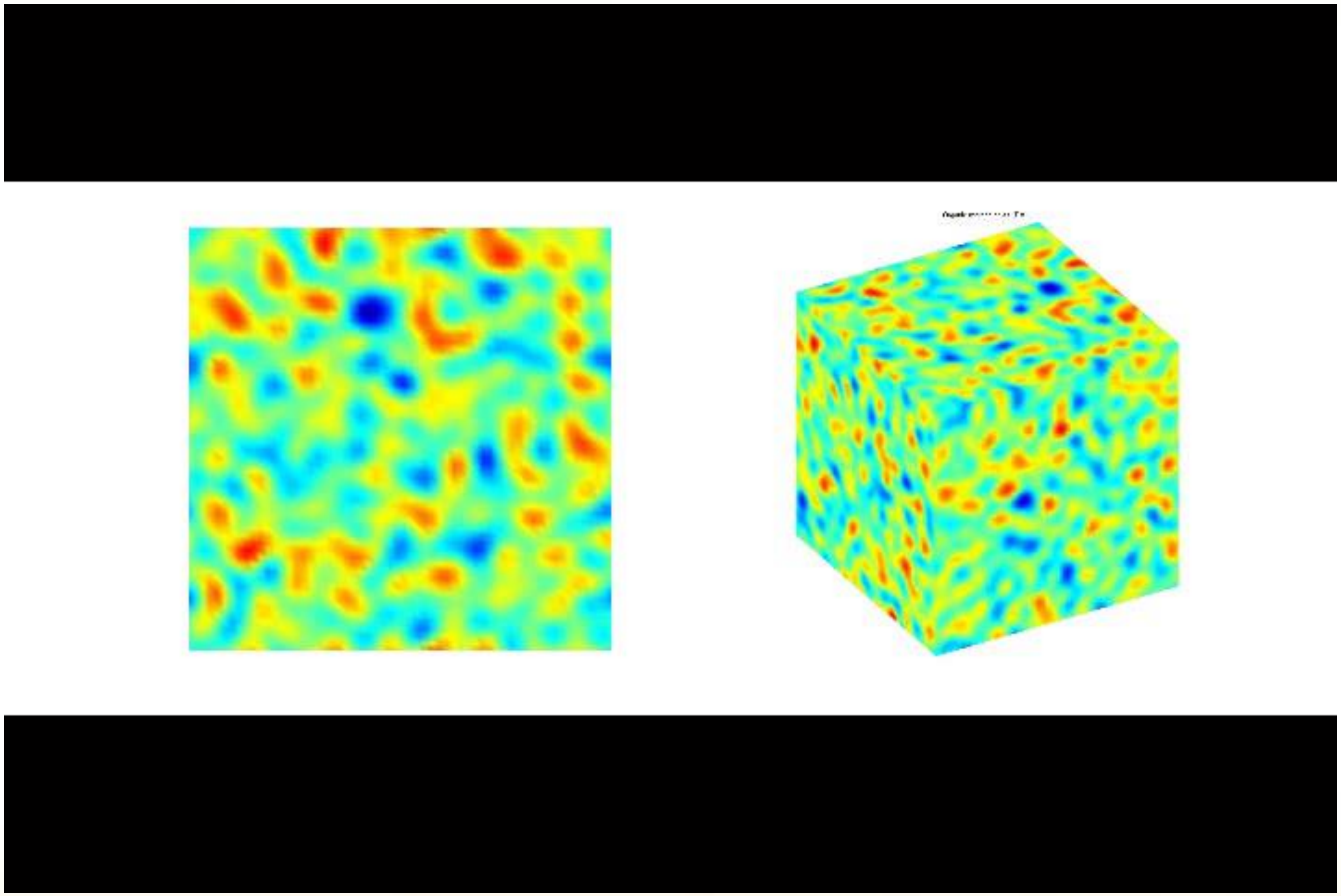
$$\frac{\partial C}{\partial t} = \nabla^2 \left( M \frac{\partial f}{\partial C} - k \nabla^2 C \right)$$

*FFT*

$$\frac{\partial \hat{C}}{\partial t} = M \lambda \left( \frac{\partial \hat{f}}{\partial C} - k \lambda \hat{C} \right)$$

$$\lambda = \frac{2 \sum \cos(2\pi k_i) - \sum 2}{(\Delta x)^2}$$

# Simulated organic morphologies



# Summary

- ✓ Spectral method has been used to numerically solve higher order differential equations
- ✓ Flory-Huggins and Allen-Cahn equations were used to simulate 3D organic morphologies

# Outline

- **Synthesis of ZnO nano/microspheres**
  - ✓ Control of ZnO morphologies
  - ✓ Effect of structure direct agents on ZnO morphologies
  - ✓ Control of uniformity, distribution, and size of ZnO spheres
  - ✓ Synthesis of ZnO nano/microspheres
- **Organic solar cells**
  - ✓ Recombination process of organic solar cells
  - ✓ Degradation mechanisms of organic solar cells
  - ✓ Simulation of 3D organic morphologies
- **Power of Words**

# Experiment of the power of words

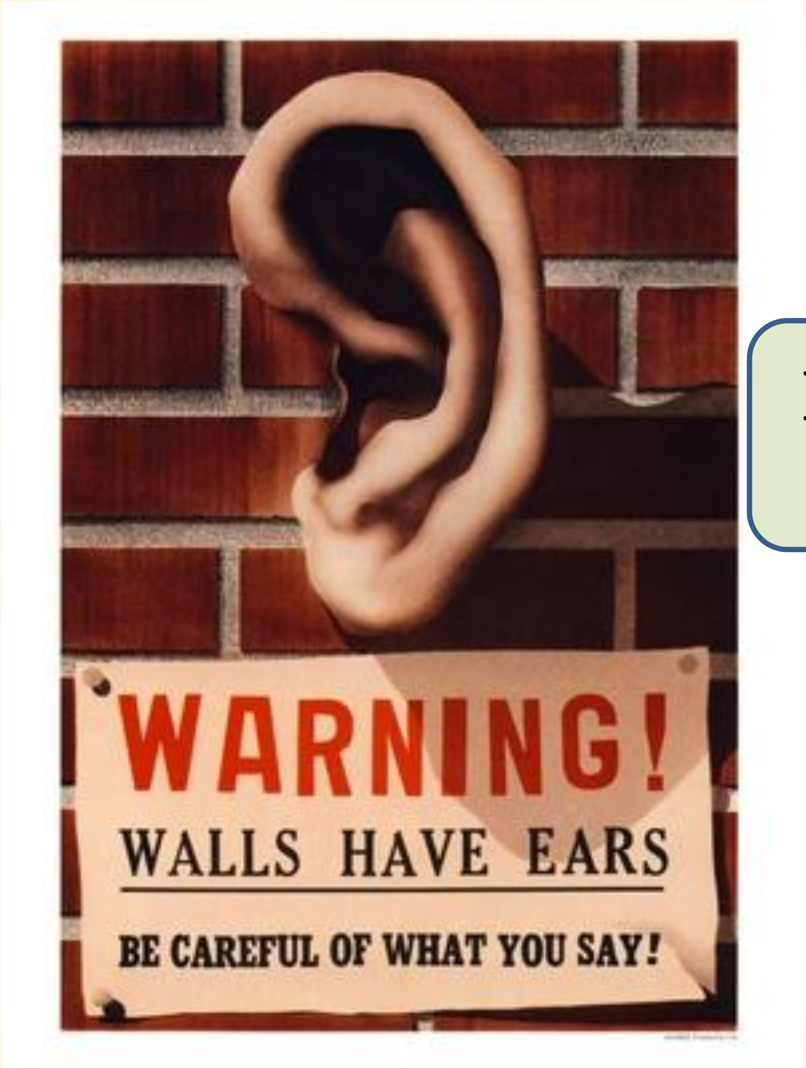
# Words

[1] In the beginning was the Word, and the Word was with God, and the Word was God. John 1:1

[1]In the beginning God created the heavens and the earth. [3] And God said, "Let there be light," and there was light. Genesis 1:1,3.

[12] For the word of God is alive and active. Sharper than any double-edged sword. Hebrew 4:12

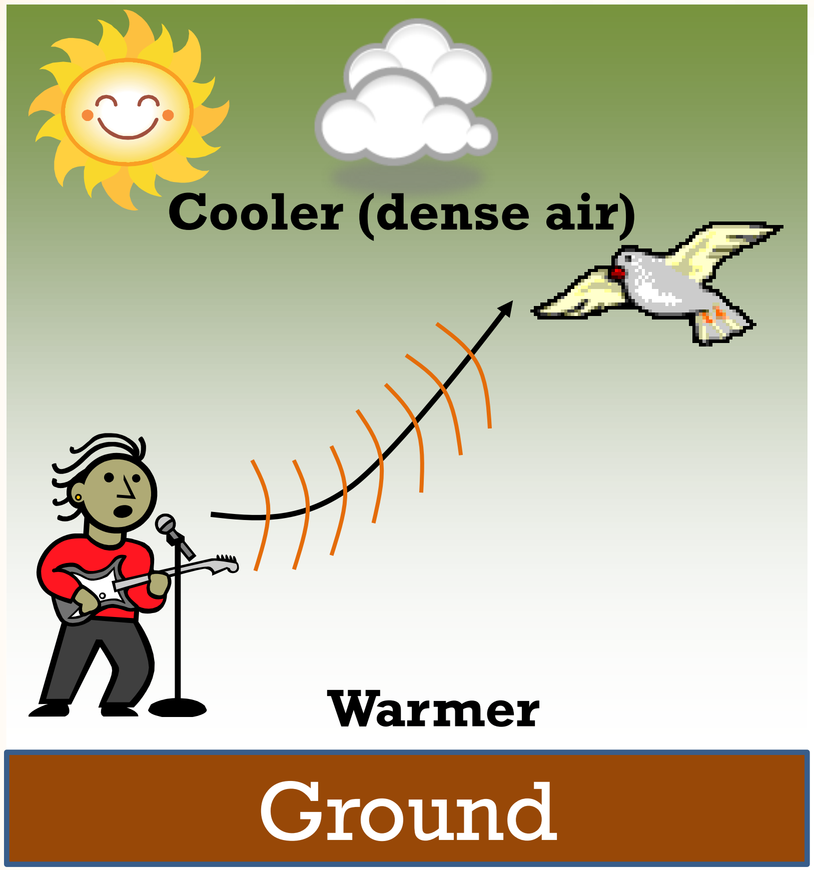
# Idiom and proverb



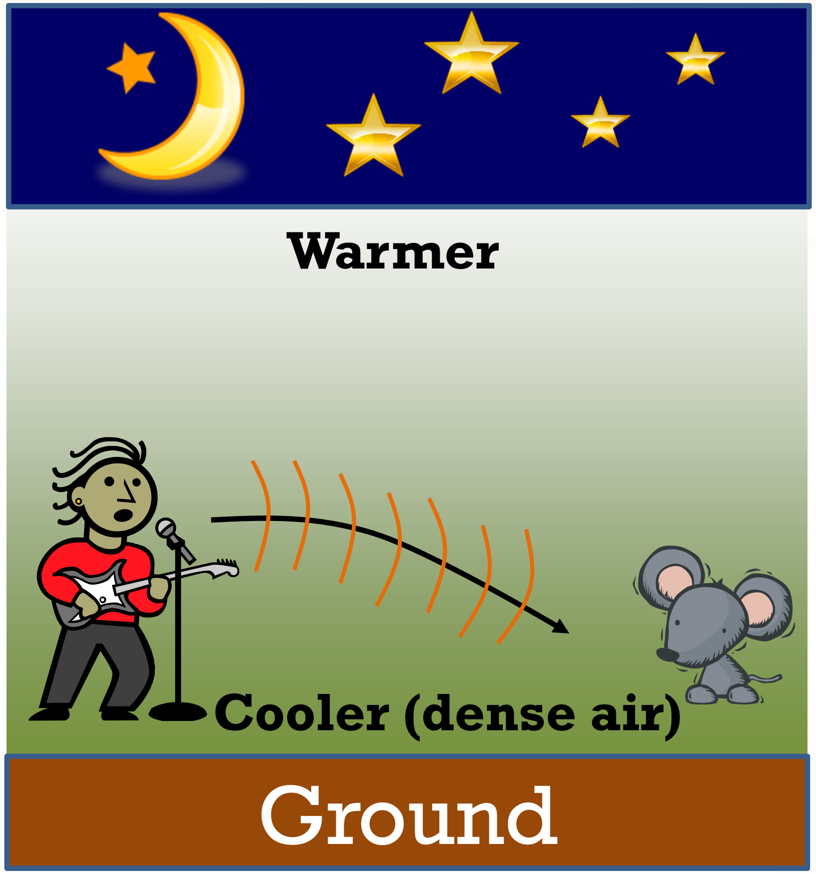

Korean proverb

Birds hear what is said by day, and rats hear what is said by night

# Prove

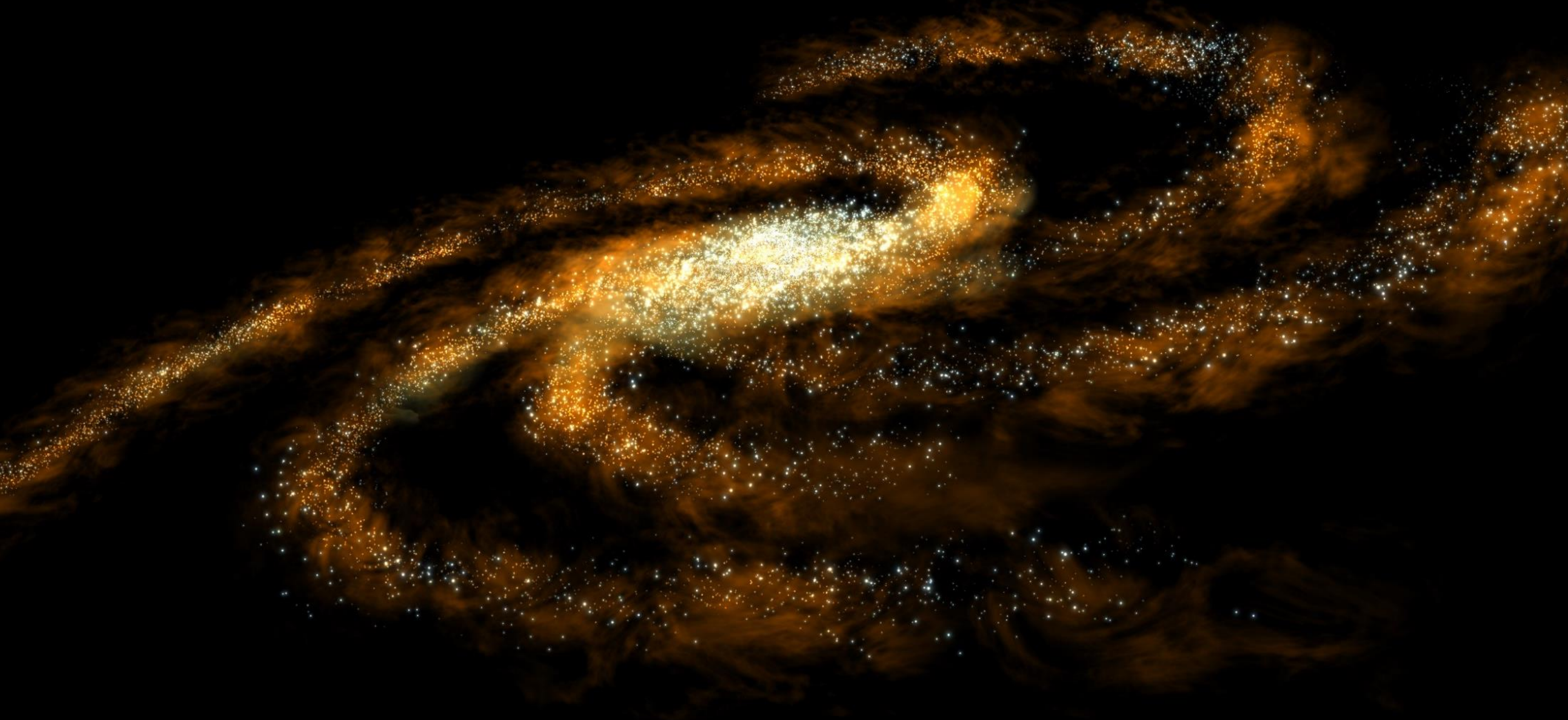



Birds hear what is said by day




Rats hear what is said by night

# Research History



# Conclusion

## **Re-search His story**