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

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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**
Outline

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• **Power of His Words**
ZnO morphologies

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

Missing morphology $\Rightarrow$ ZnO sphere

ZnO structures

Noncentrosymmetric ZnO structure

\[ a = 3.247 \text{ Å} \]
\[ b = 5.207 \text{ Å} \]

\[ \frac{b}{a} = 1.6 \]

ZnO structures (Cont.)

ZnO has a noncentrosymmetric crystal structure

Scientific reports, Vol 2, pp 587
ZnO structures (Cont.)

ZnO has a noncentrosymmetric crystal structure

Strong spontaneous polarization

Scientific reports, Vol 2, pp 587
ZnO structures (Cont.)

ZnO has a noncentrosymmetric crystal structure

Strong spontaneous polarization

Surface charge on the (0001) plane

Scientific reports, Vol 2, pp 587
Hydrothermal synthesis of ZnO

Autoclave reactor

Zinc acetate: $\text{Zn}((\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$

Ammonia hydroxide: $\text{NH}_4\text{OH}$
Hydrothermal synthesis of ZnO

Zn cation \( \text{Zn}(\text{NH}_3)_4^{2+} \)
Zn anion \( \text{Zn}(\text{OH}_3)_4^{2-} \)

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

\[ [\text{NH}_3]_{\text{TOT}} = 10.00 \text{ mM} \]
\[ [\text{Zn}^{2+}]_{\text{TOT}} = 23.00 \text{ mM} \]

\( \text{ZnO polar surface} \Rightarrow \text{preferential growth} \)

ZnO with different pH values

Zinc acetate

<table>
<thead>
<tr>
<th>pH</th>
<th>23mM</th>
<th>50mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td><img src="a.png" alt="Image" /></td>
<td><img src="d.png" alt="Image" /></td>
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<tr>
<td>11</td>
<td><img src="b.png" alt="Image" /></td>
<td><img src="e.png" alt="Image" /></td>
</tr>
<tr>
<td>12</td>
<td><img src="c.png" alt="Image" /></td>
<td><img src="f.png" alt="Image" /></td>
</tr>
</tbody>
</table>
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

\[
\begin{align*}
\text{N} & \quad \delta^- \\
\text{H}_2\text{N} & \quad \delta^+ \\
\text{C} & \quad \delta^+ \\
\text{NH}_2 & \quad \delta^+ \\
\text{O} & \quad \delta^- \\
\end{align*}
\]

pH=10

With Urea

With ethanol

pH=11

pH=12

ethanol

\[
\begin{align*}
\text{H} & \quad \delta^+ \\
\text{H} & \quad \delta^+ \\
\text{C} & \quad \delta^- \\
\text{C} & \quad \delta^- \\
\text{C} & \quad \delta^- \\
\text{O} & \quad \delta^- \\
\text{H} & \quad \delta^+ \\
\text{H} & \quad \delta^+ \\
\text{H} & \quad \delta^+ \\
\end{align*}
\]
Temporal evolution of ZnO
Temporal evolution of ZnO
Temporal evolution of ZnO
Temporal evolution of ZnO
Control of size and distribution of ZnO spheres

Urea (1):Ethanol (1)

Urea (1):Ethanol (1.25)
X-ray diffraction measurement

(a)

(b)

(002)

Intensity (arb. units)

2θ (deg.)

ZnO (100)

ZnO (101)

ZnO (102)

ZnO (110)

ZnO (103)

ZnO (200)
Confocal PL of ZnO spheres

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
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 His Words**
Current state-of-the-art solar cells

- **Cost Efficiency**
  - Current state of the art solar cells:
    - Semiconductor PV (GaAs, Si, GaN, ...)
    - Thin Film PV (CIGS, a-Si, CdTe, ...)
    - New generation PV (Organic, Inorganic, ...)

Cost Efficiency Diagram:

- X-axis: Cost
- Y-axis: Efficiency

- Semiconductors (GaAs, Si, GaN, ...)
- Thin Films (CIGS, a-Si, CdTe, ...)
- New Generations (Organic, Inorganic, ...)

Efficiency increases as you move up the y-axis.
Organic solar cells

Absorption of polymer

Transparent solar cells

PTB7
Fabrication of organic solar cell

Polymer  \[\text{PCBM fullerene}\]  Donor

Accept
PCDTBT:PCBM solar cells

Recombination processes

Exciton generation

\[ \tau_{\text{exciton}} \approx \text{nanoseconds} \]
Recombination processes

Heterojunction bipolar
Hetero-interface
Dissociation center
Nanoscale morphologies

τ_{exciton} = \sim 10 \text{ ns}

Exciton diffusion length

L_{exciton} = \sqrt{D \tau_{exciton}}
\sim 10 nm

photon
---

+ bound e/h

Dissociation center

Nanoscale morphologies

Heterojunction bipolar

p-contact

n-contact

Light

bound e/h

polymer

Fullerene

Top electrode

Transparent electrode
Recombination processes

- photons
- free electron (n-contact)
- free hole
- p-contact

Diagram:
- Top electrode
  - polymer
  - Fullerene
- Transparent electrode
- Light
Recombination processes

Langevin recombination

\[ R = k_r (np - n_i^2) \]

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

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

Light (hv)

Reducing charge transport efficiency
Creating defects and trap centers
Influence of photo-oxidation on charge transport

Photo-oxidation

trapped
Degradation of organic solar cells

**Polymers**

PTB7

**PCBM**

PTB7

PCBM

ITO

Al
Degradation of organic solar cells

![Stack Diagram of Organic Solar Cell](image)

- Electrode
- TiO₂
- PTB7:PCBM
- ITO
- Glass

![Graph showing Normalized Efficiency over Time](image)

- **PTB7/PC₇₁BM**
  - With TiOₓ (solid line)
  - Without TiOₓ (dotted line)

- Normalized Efficiency
  - Time (Days)

- With TiOₓ: ~25%
- Without TiOₓ: ~50%
Role of TiO$_2$ for organic solar cells

Sol-Gel processed TiO$_x$

Electrode

Organic blends

ITO

Glass

Redox process

CO$_2$ (gas)

H$_2$O(gas)

TiO$_2$
Effect of sealing of organic solar cells on degradation

- PTB7:PCBM/TiOx
  - Sealed, in glove box
  - Sealed, in air
  - Unsealed, in air

Normalized Efficiency vs. Time (Days)

- 32%
- 41%
- 99%
Comparison of UV-VIS absorption

Sealed PTB7/PCBM in air

PTB7/PC$_{71}$BM/TiO$_x$
With sealant glass in air
- As cast
- After 10 days
- After 20 days

Not sealed PTB7/PCBM in air

PTB7/PC$_{71}$BM/TiO$_x$
Without sealant glass in air
- As cast
- After 10 days
- After 20 days
Absorption of PTB7 and PCBM

Not sealed PTB7/PCBM in air

PTB7/PC_{71}BM/TiO_x
Without sealant glass in air

- **As cast**
- **After 10 days**
- **After 20 days**

Absorption (arb. units)
Wavelength (nm)

PTB7
PCBM
Degradation mechanism for organic solar cells

Sealed PTB7/PCBM in air

PTB7

PCBM

O₂

TiO₂

Electrode

Organic blends

ITO

Glass

Diagram showing the degradation mechanism of organic solar cells with PTB7 and PCBM layers.
Degradation mechanism for organic solar cells

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

7 days mixing

P3HT

PC_{71}BM
Effect of uniform morphologies

Light absorption

JV characteristics

<table>
<thead>
<tr>
<th>X Axis Title</th>
<th>Y Axis Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 400 500 600 700 800</td>
<td>0.10 0.15 0.20 0.25 0.30 0.35 0.40</td>
</tr>
<tr>
<td>3 days 1 day 5 days 7 days</td>
<td>-12 -10 -8 -6 -4 -2 0 2 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>V(Volt)</th>
<th>J(mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 0.2 0.4 0.6</td>
<td>-0.2 0.0 0.2 0.4</td>
</tr>
</tbody>
</table>

Light absorption and JV characteristics show the effect of uniform morphologies.
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

Polymer: Fullerene

\[ dG = dH - TdS \]

- \( G \): 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

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

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

Composition of polymer

\[ 0 \quad C_A \quad C_x \quad C_B \quad 1 \]
Numerical simulation of partial differential equations

- Finite difference 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
M. Mehra et al., Comparison between different numerical methods for discretization of PDEs.
Spectral methods

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

\( \Phi_k(x) \); interpolating function

Polynomial fitting

max error = 5.9001

Trigonometric fitting

max error = 0.017523

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

\[ e^{ikx} = \cos(kx) + i \sin(kx) \]
1D Allen-Cahn equation

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

\[ \text{FFT}(u_j) \equiv \hat{u}_k \]

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

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

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

Inverse FFT

\[ u = \text{iFFT}(\hat{u}) \]
3D Allen-Cahn Equations

Flory-Huggins type of free energy

\[ f = \frac{RT}{\nu_{\text{site}}} \left( \frac{C_A}{m_A} \ln C_A + \frac{C_B}{m_B} \ln C_B + \chi_{AB} C_A C_B \right) \]

Allen-Cahn Equation

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

Forward Fourier Transform (FFT)

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

\[ \lambda = \frac{2 \sum \cos(2\pi k_i) - \sum 2}{(\Delta x)^2} \]
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.
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• **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
Conclusion

Re-search His story