Morphology and electronic alignment of the Poly(3-hexylthiophene)/ZnO interface

Switchable surface chemistry on ferroelectric surfaces

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Photovoltaics

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Chemical Engineering, Yale

Funding: NSF SOLAR program

Catalysis

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Physics, Yale

Experimental collaborators:
Matt Herdiech & Eric Altman
Chemical Engineering, Yale

Funding: Toyota Motor Engineering & Manufacturing North America, Inc.
Some materials configurations for photovoltaics

Conventional planar
• High efficiency
• Expensive & fragile
• Limited active interface

Bulk heterojunction
• Modest efficiency (~5 %)
• Cheap & easy to manufacture
• Carrier transport issues

Ordered heterojunction
• Good efficiency
• Great carrier transport
• Difficult to realize: nm scale alignment
Self-assembly of polymer/nanowire

ZnO nanowires (NW): hexagonal facets, well-defined (10\(\overline{1}0\)) surfaces
P3HT polymers

Small diameter NW:
• polymer well ordered
• coaxial with nanowire

P3HT/ZnO interface

Energy alignment for separated P3HT & ZnO

backbone
side chain

ZnO

P3HT

Energy levels:
- LUMO: 1.95 eV
- HOMO: 3.35 eV
ZnO surface

ZnO nanowire surface: (10\bar{1}0)

Which surface direction does P3HT prefer?
P3HT binding & strain energies

PWSCF (Quantum Espresso)
Plane wave basis
Ultrasoft pseudopotentials
PBE GGA functional
Frenkel-Kontorova model
1D competition of strain & periodic binding potential

Dynamics of this model is very hard...

But (despite what I learned in grad school), the ground state of this model is solved with a simple efficient algorithm.

Frenkel-Kontorova model

\[ E = \frac{1}{2} \sum_i k (x_{i-1} - x_i - l_0)^2 + \sum_i V(x_i) \]

Red is optimum distance for P3HT

Within 25% strain: only matches are x, y & xy directions
Ground states

- Valid for surface or large diameter NW
- Smaller diameters: if curvature energy > 0.4 eV, can change alignment

Alignments for flat ZnO surface
Fixed morphology versus binding

Helical wrapping preferred for almost any binding energy

This is for very large nanowires
Can curvature make for coaxial?
Curvature effect 1

Elementary elastic effect: curving polymer backbone costs energy

Actually irrelevant for ~20 nm nanowires...
Curvature effect 2

Curved polymer makes binding ends closer:

→ effective change of periodicity of potential
→ has significant energetic effect

Easy to model: change lattice constant in Frenkel-Kontorova
Final morphology prediction

Helical $\rightarrow$ coaxial transition predicted

Seems to agree with experiment
Electronic structure (PBE0)

Clean ZnO, clean linker

Clean ZnO, hydrogenated linker

Bad alignment

Good alignment

S linker is open shell
Accepts electrons from ZnO
(hole dopes)
Electronic structure

Hydrogenated ZnO, clean linker

Hydrogenated ZnO and linker

Good alignment

Bad alignment
Thermodynamic phase diagram

Structure, stability and band alignment

$E_{\text{tot}} - n x E_H$ [eV]

<table>
<thead>
<tr>
<th>$\mu - \mu_0$ [eV]</th>
<th>Structure</th>
<th>Stability</th>
<th>Alignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu = \mu_0 - 1.45$</td>
<td>structure</td>
<td>$&lt; -1.45$ eV</td>
<td>bad</td>
</tr>
<tr>
<td>$\mu = \mu_0 - 0.26$</td>
<td>structure</td>
<td>$[0, -0.26)$ eV</td>
<td>good</td>
</tr>
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</table>

$\mu_0$ : H chemical potential at $T=0, P=0$
$\mu_0 - 0.26$ eV: $T=373$K and $P=1$ atm
$\mu_0 - 1.45$ eV: $T=1773$K and $P=1$ atm
Summary 1

• Curvature effects can align polymer/nanowire coaxially

• FK model a cheap and useful model for these systems

• Covalent tethering of polymer makes interfacial chemistry and passivation critical --- difficult extra materials problem to deal with...

• Open circuit voltage for good alignments are ~ 1.0 eV which is as good or better than physisorbed P3HT (0.4-0.8 eV)
Catalysis on ferroelectrics: outline

• Overview of precious metal catalysts & problems
  • Overview of ferroelectrics
  • Theoretical approach: DFT, NEB
  • Sampling of results
  • Proposed NO\textsubscript{x} reduction cycle
  • Preliminary results on key energy barriers
• What’s next
Current Methods for NO$_x$ Reduction

(Primary focus is on automotive applications)

- Precious metals catalysts -- expensive

- Some key reactions
  - oxidize CO $\rightarrow$ CO$_2$
  - reduce NO$_x$ $\rightarrow$ N$_2$ + O$_2$

- Current catalysts bind O too strongly
  - Air:fuel ratio must be $\approx$ stoichiometric (no excess O$_2$)
  - Some fuel/CO used to remove O from catalyst
**Sabatier Principle**

Catalyst-molecule interaction must be “just right”: not too strong, not too weak

Standard volcano plot

Strong atomic adsorption:
→ Barrier low, fast dissociation
→ But atoms never come off!

Weak atomic adsorption:
→ Barrier high, very slow reaction

Compromise situation

Formic acid decomposition
Outline

• Overview of precious metal catalysts & problems

• **Overview of ferroelectrics**

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• What’s next
What is a ferroelectric?

- Two stable polarization states.
- Switch with Electric field.
What is a ferroelectric?

- Two stable polarization states.
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PbTiO$_3$
A ferroelectric: PbTiO$_3$

- Perovskite Structure
- Ferroelectric
- Strong Polarization
Ferroelectrics & surface chemistry

• 2 polarizations $\rightarrow$ 2 surfaces (for the price of 1)
• Control with $E$ field
• Possible Uses:
  – Bind/Release Molecule
  – Change surface electronic states $\Rightarrow$ affect catalysis
  – Chemical Sensing
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\[ P^- + + + P^- + + + P^- - - - P^- - - - \]
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DFT modeling

• Plane wave basis
• Ultrasoft (Vanderbilt) pseudopotentials
• 15 Å vacuum
• Dipole Correction

→ Converge binding energies to ~ 0.01 eV

PWSCF (Quantum Espresso)
Cold smearing
8x8 k-point sampling per 1x1 cell
PW91 GGA
30 Ryd cutoff
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### What we calculated (so far)

<table>
<thead>
<tr>
<th></th>
<th>NO</th>
<th>NO dis.</th>
<th>O₂</th>
<th>O₂ dis.</th>
<th>N₂</th>
<th>N₂ dis.</th>
<th>N</th>
<th>O</th>
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<tbody>
<tr>
<td>PbTiO₃ (PbO term.)</td>
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<td>PbTiO₃ (Stable)</td>
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<td>RuO₂ / PbTiO₃</td>
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<td>✓</td>
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</table>
NO on RuO$_2$ / PbTiO$_3$

Positive

Paraelectric

Negative

1.2 eV

0.3 eV

-1.4 eV

2.0 eV

1.8 eV

1.4 eV
O₂ on RuO₂ / PbTiO₃

Positive

Paraelectric

1.58 eV

0.88 eV

1.98 eV

1.14 eV
O₂ on RuO₂ / PbTiO₃

Neg. polarization:

- weak interactions
- O + O → O₂ favored
- O₂ weakly physisorbed
2 $N$ or $N_2$?

<table>
<thead>
<tr>
<th>Surface</th>
<th>$N_2$ binding</th>
<th>N + N binding</th>
<th>N$+$N$\rightarrow$N$_2$ ?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive</td>
<td>0.14</td>
<td>-2.02</td>
<td>Yes</td>
</tr>
<tr>
<td>Paraelectric</td>
<td>0.62</td>
<td>-3.13</td>
<td>Yes</td>
</tr>
<tr>
<td>Negative</td>
<td>0.26</td>
<td>-4.38</td>
<td>Yes</td>
</tr>
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</table>

- N$+$N $\rightarrow$ $N_2$ always favored
- $N_2$ is weakly physisorbed
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• What’s next
O+O strongly bound ~ 2 eV: hard to release

O+O unstable ~ -0.7 eV relative to gas phase

O₂ weakly bound ~ 0.2 eV relative to gas phase: easy to release
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• Some key energy barriers
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NO dissociation: positive RuO$_2$/PbTiO$_3$

- Barrier = 1.3 eV
- Like transition metals: transition state is $\approx$ 2 separate atoms

Is 1.3 eV big or small?
Ru (0001) is active for NO dissociation and has barrier of 1.2-1.3 eV
# Polarization dependent barriers

**NO dissociation process on RuO$_2$ / PbTiO$_3$**

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<tbody>
<tr>
<td>NO $\rightarrow$ N + O barrier</td>
<td>1.31</td>
<td>2.25</td>
<td>3.04</td>
</tr>
<tr>
<td>Adsorption energy of N + O</td>
<td>-1.2</td>
<td>-0.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**N + N $\rightarrow$ N$_2$ process**

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<tr>
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</thead>
<tbody>
<tr>
<td>Barrier</td>
<td>0.51</td>
<td>---</td>
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What’s next

1. Obviously calculate more barriers → kinetic Monte Carlo

2. Thermodynamics of monolayer RuO$_2$ on PbTiO$_3$
   Stays catalytic?
   Diffuses into bulk?
   What is its stoichiometry?

3. Poisoning effects of other gases (CO, CO$_2$, H$_2$O, …)

4. Other ideas and broader point:
   can remove “Sabatier compromise” with ferroelectric…. 
Why Ru? Other metals?

- Chose RuO$_2$ because bulk RuO$_2$ is known “regular” NO catalyst

- Regular catalyst: has a “just right” interaction with NO

- Not stuck to “just right” interactions!

- Can choose different metals which may be more optimal on a ferroelectric surface