CONTROLLING SURFACE PROPERTIES OF METAL OXIDE TO IMPROVE SOLAR CELL EFFICIENCY

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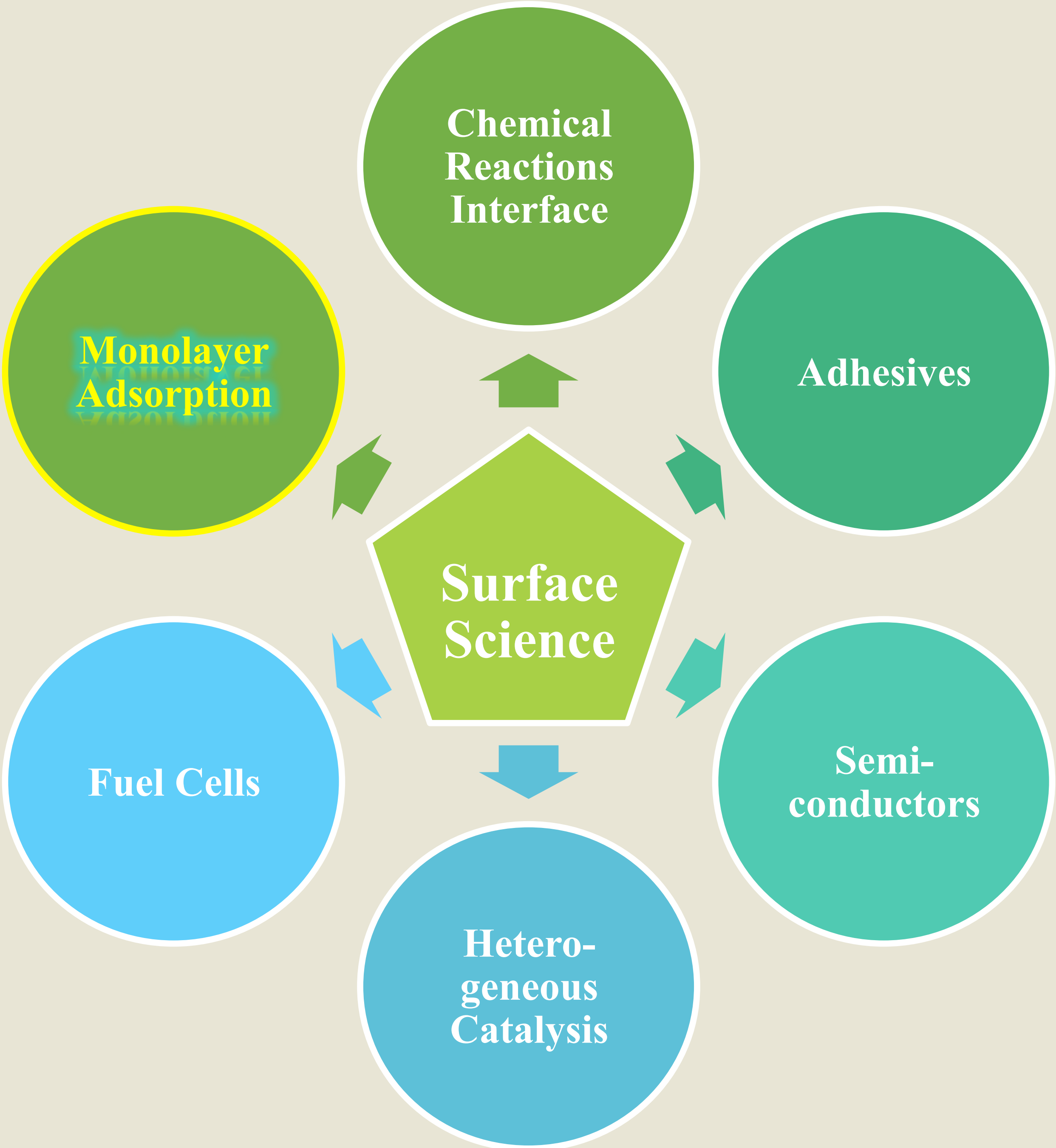
Renewable Energy in West Virginia

Physisorbed

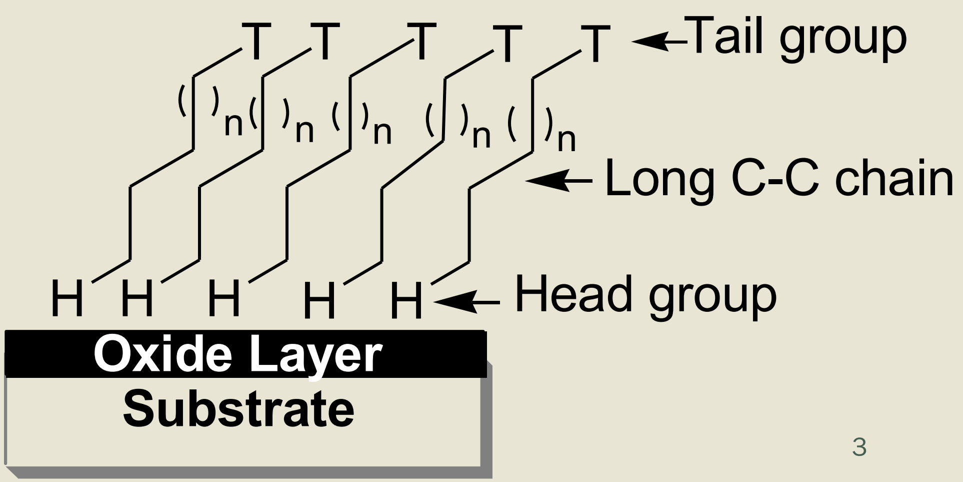
Langmuir

Self Assembled



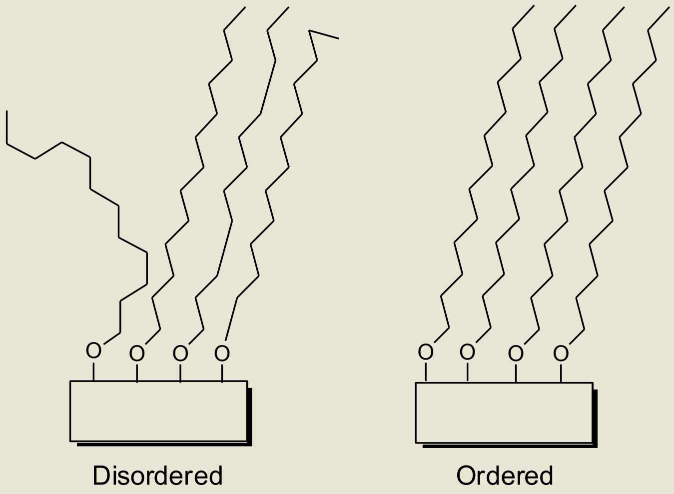
Self-Assembled Monolayers

- A Self-Assembled Monolayer (SAM) is a monomolecular film of an organic compound on a solid surface
- SAMs exhibit
  - *High degree of orientation*
  - *Molecular order*
  - *Close packing*
- Self-Assembled Monolayers are flexible because the head or tail groups can be varied
- SAMs have been able to control corrosion



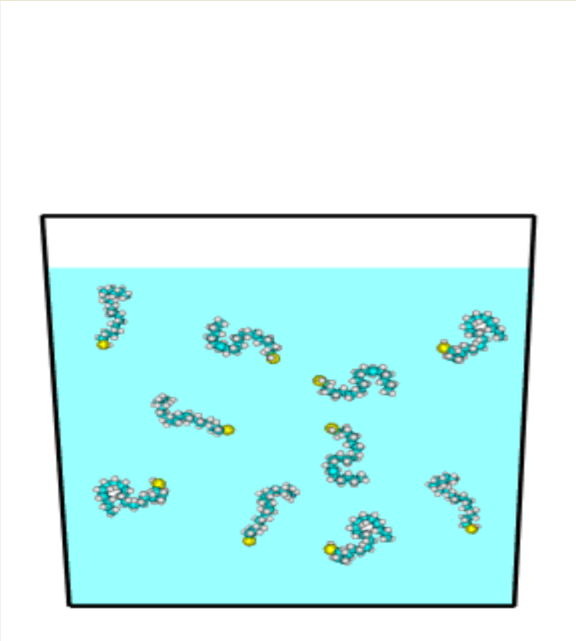
SAM Formation

- There are two types of films: ordered and disordered
  - *Ordered-C-C chains have all- trans conformations*
  - *Disordered-C-C chains have some gauche conformations*
- A long alkyl chain, greater than 12 carbons, is commonly used in SAMs
  - *Longer chain lengths tend to form all- trans conformations in the alkyl chain*
- Several factors affect the formation and packing density of monolayers
  - *Nature and roughness of substrate*
  - *Head group*
  - *Tail group*
  - *Solution concentration*



Film Deposition Method

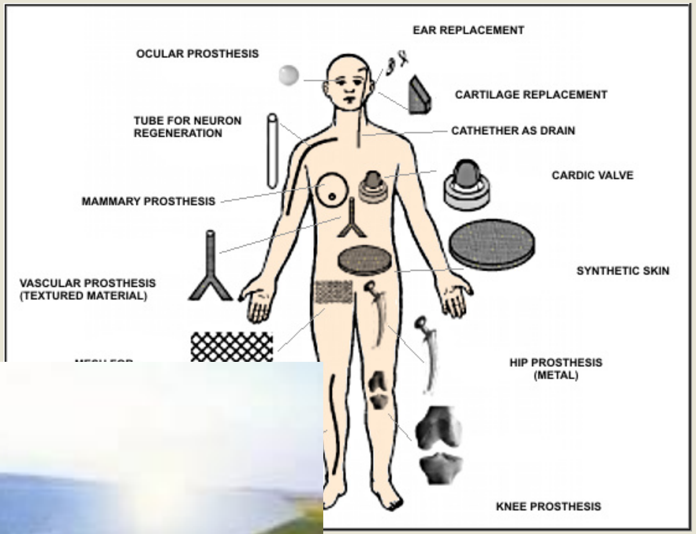
- SAMs provide one of the easiest ways to efficiently obtain closed packed films
  - *Small Concentration of the solute*
  - *Easy deposition methods*

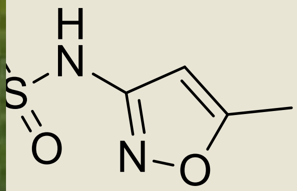


- http://marvin1.pc.ruhr-uni-bochum.de/

Self-Assembled Monolayer Applications

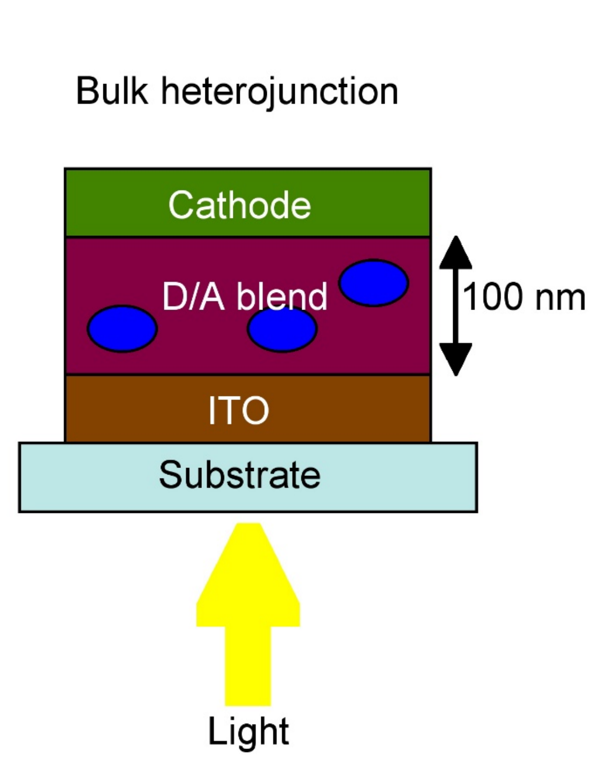
- Corrosion barrier
  - *Biomaterial*
- Pharmaceutical applications
  - *Polymorph*
- Solar cells
  - *Work function*





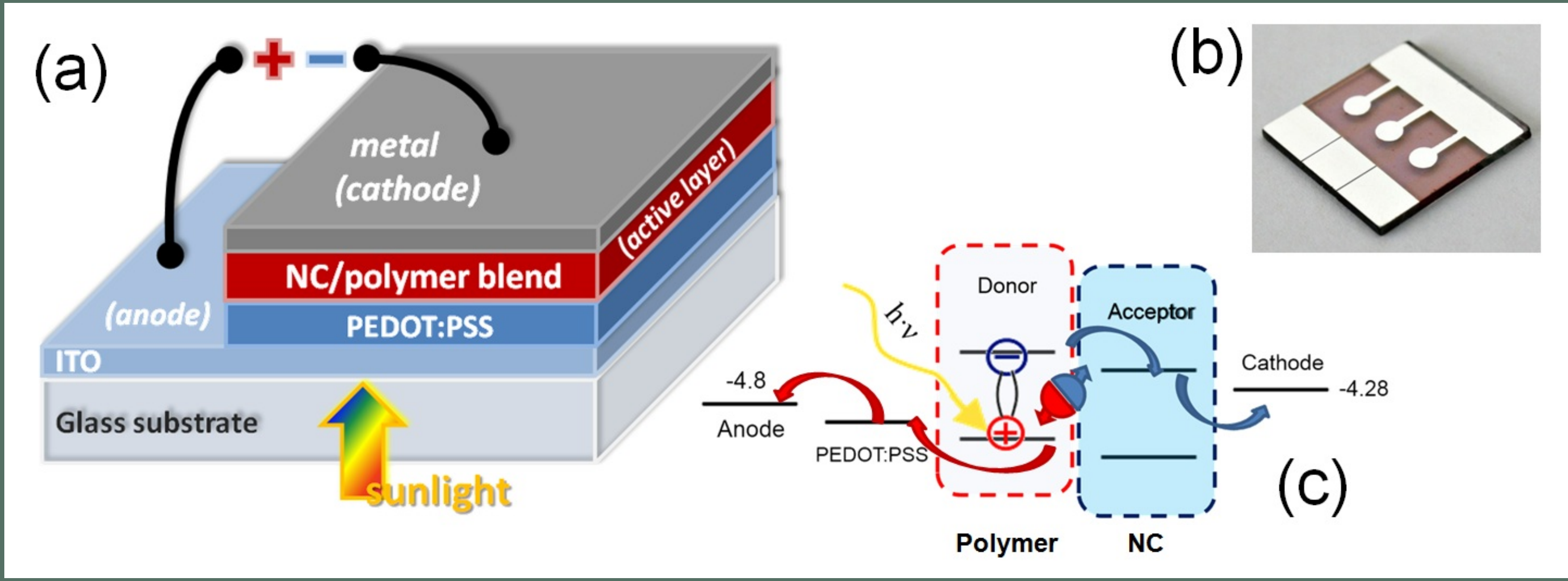
Solar Cells

- The most common solar cells are made of silicon
  - *20% energy efficiency*
  - *Expensive*
- Research in solar cells
  - *Organic/polymer based solar cells*
  - *Dye sensitized solar cells*
    - Lightweight
    - low-cost
    - Large area processability



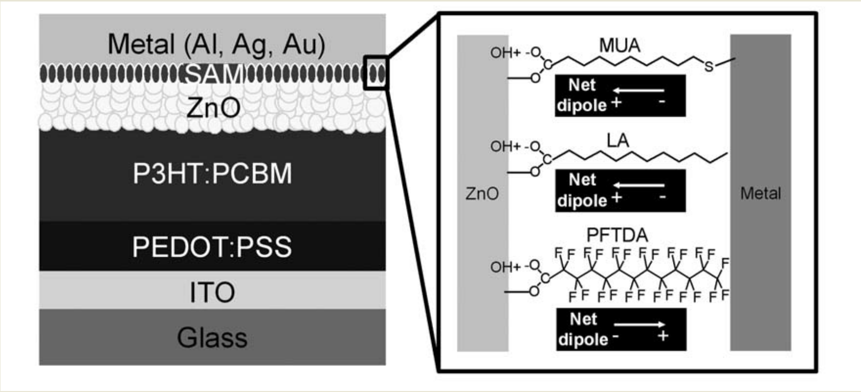
cnx.org

Heterojunction Solar Cells



Heterojunction Solar Cells

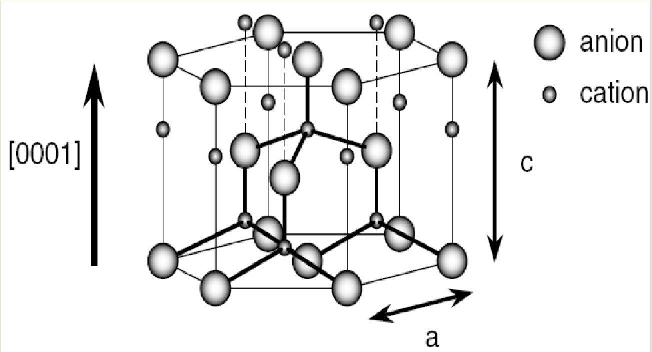
- Organic photovoltaic cells are great interest of scientists
  - *Low-cost generation*
  - *Easy processability*
  - *Alternative to high cost silicon based solar cells*
- Polymer solar cells
  - *Large scale production*
  - *Flexibility*
  - *Low-temperature operation*
- Performances of organic solar cells are highly dependent of:
  - *Morphology of active layers*
  - *Metal oxide layers*
- Inverted-type bulk heterojunction solar cells can be fabricated using different ZnO interlayers
  - *investigate the performances*
  - *Energy efficiencies*



Appl. Phys. Lett. 92, 193313 (2008)

Zinc Oxide Nanoparticles

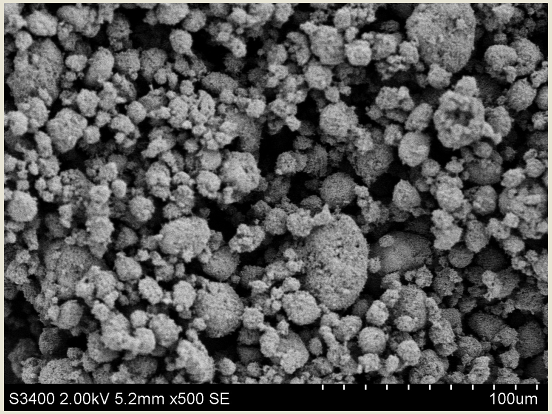
- Useful properties of zinc oxide (ZnO):
  - *Wide band gap semiconductivity (~3.3 eV)*
  - *High electron mobility*
  - *Stable hexagonal wurtzite structure*
- Applications in solar cells, energy-saving windows, antimicrobial textiles, chemical sensors, ultraviolet (UV) coatings, and corrosive-resistant coatings



http://www.grin.com/en/doc/273704/growth-and-characterization-of-zinc-oxide-and-pzt-films-for-micromachined

Project Goal

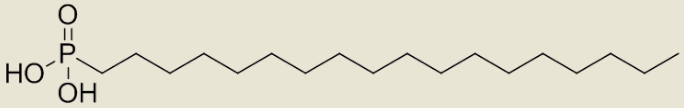
- Zinc oxide nanoparticles were modified with SAMs
  - *Phosphonic acids*
  - *Spectroscopy characterization*
    - Work function tuning



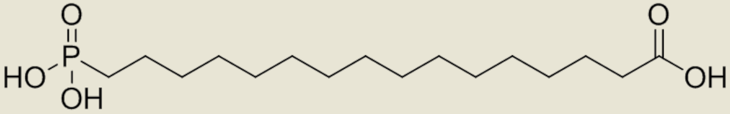
100 μm

Organic Acids

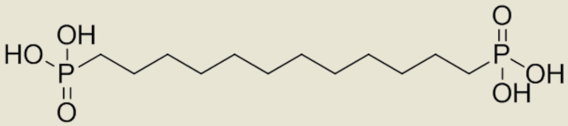
- Phosphonic Acid
  - *More stable on many metal oxide surfaces*
  - *Octadecylphosphonic acid (ODPA)*
    - *Methyl-terminated*



  - *16 – phosphonohexadecanoic acid (COOH-PA)*
    - *Carboxylic acid-terminated*



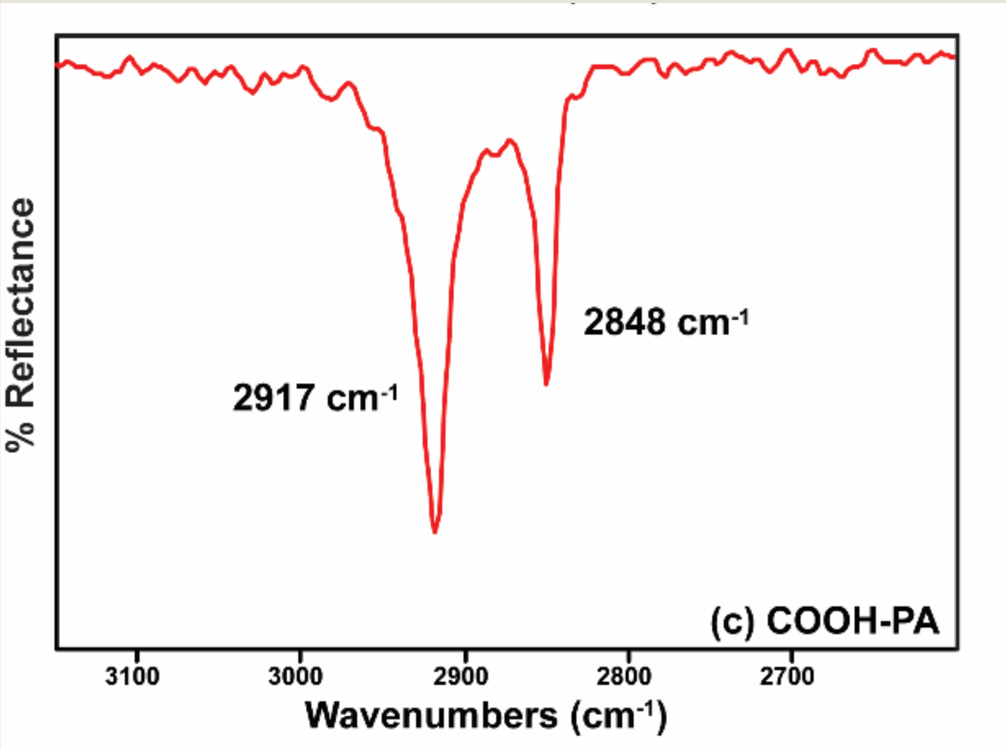
  - *(12-phosphonododecyl)phosphonic acid (Di-PA)*
    - *Phosphonic acid-terminated*



Thin Film Formation

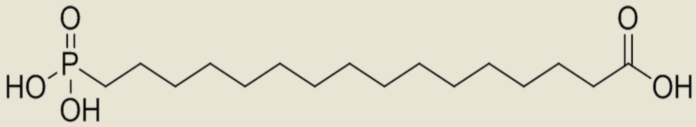
- Nanoparticles: 0.35 g ZnO (100 nm size averaged) was dissolved in 30 mL tetrahydrofuran (THF) and sonicated
- Organic acids: 0.09, 0.045, 0.02, 0.01 mmol of each acid was dissolved in THF and sonicated
- Solutions were combined and further sonicated
- Left stirring at room temperature for 24 hours
- After modification, samples were rinsed, sonicated in THF for 20 minutes, and filtered

Chemisorbed Phosphonic Acid Monolayers on ZnO Surface

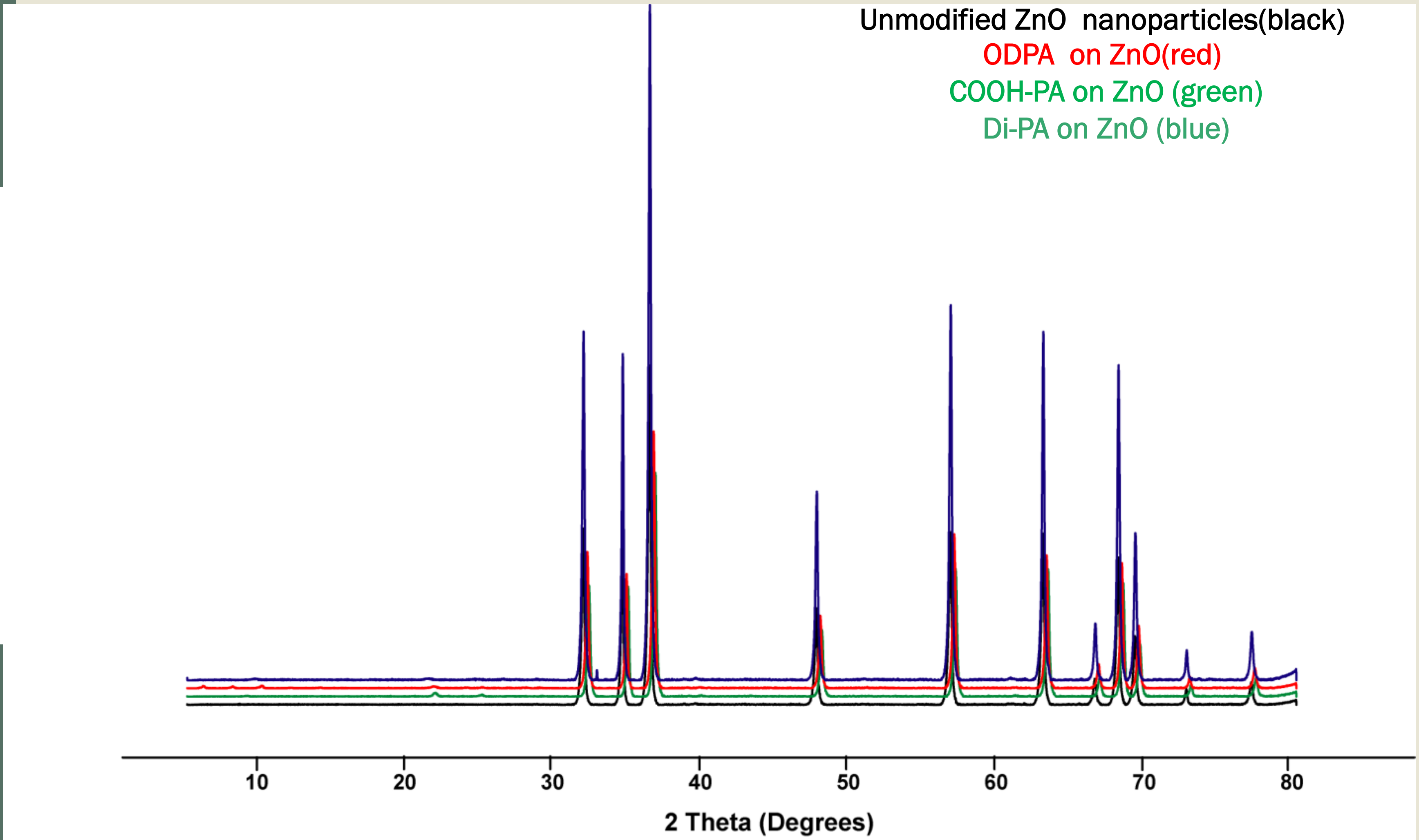


Stable – resilient to solvent rinses and sonication

COOH-PA after deposition on the surface



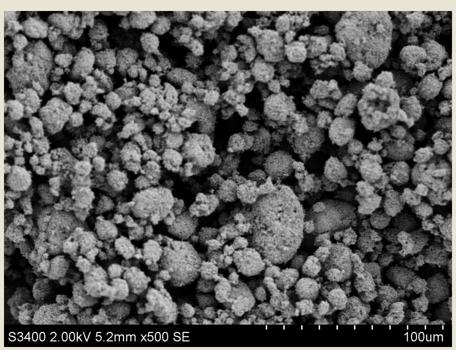
PXRD: Presence of Organic Materials



Thanks to Duquesne University for allowing us to have access to this instrument

Scanning Electron Microscope (SEM)

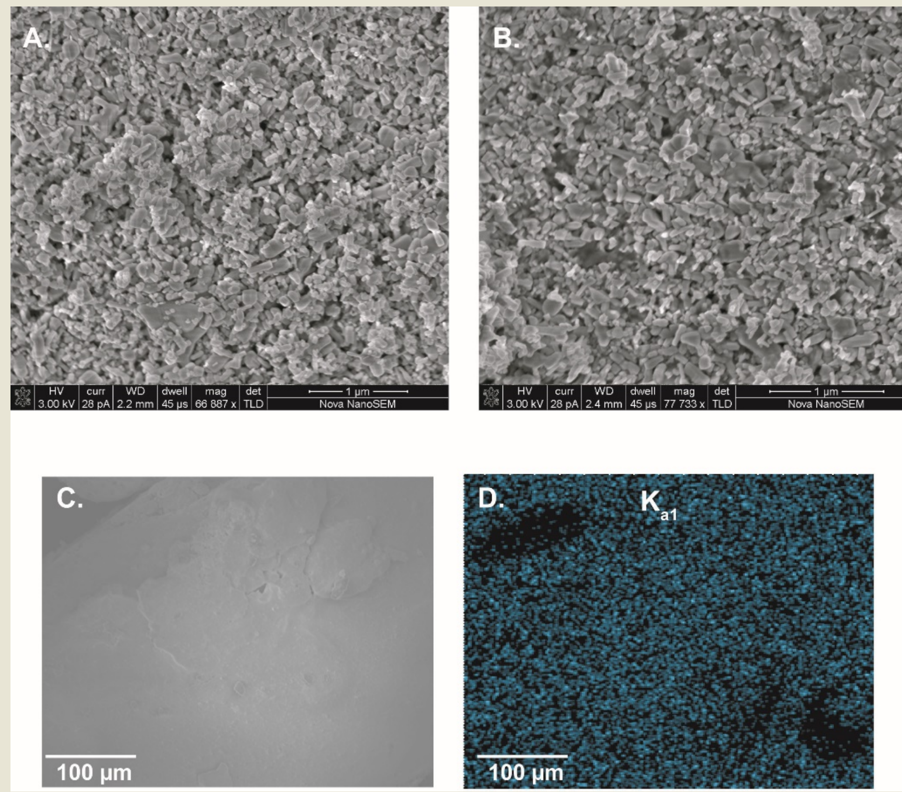
Modifications	Average Particle Size (nm)	Particle Distribution (±nm)
ZnO	106	27
ZnO – ODPA	145	53
ZnO – COOH-PA	161	61
ZnO – Di-PA	194	83



ZnO

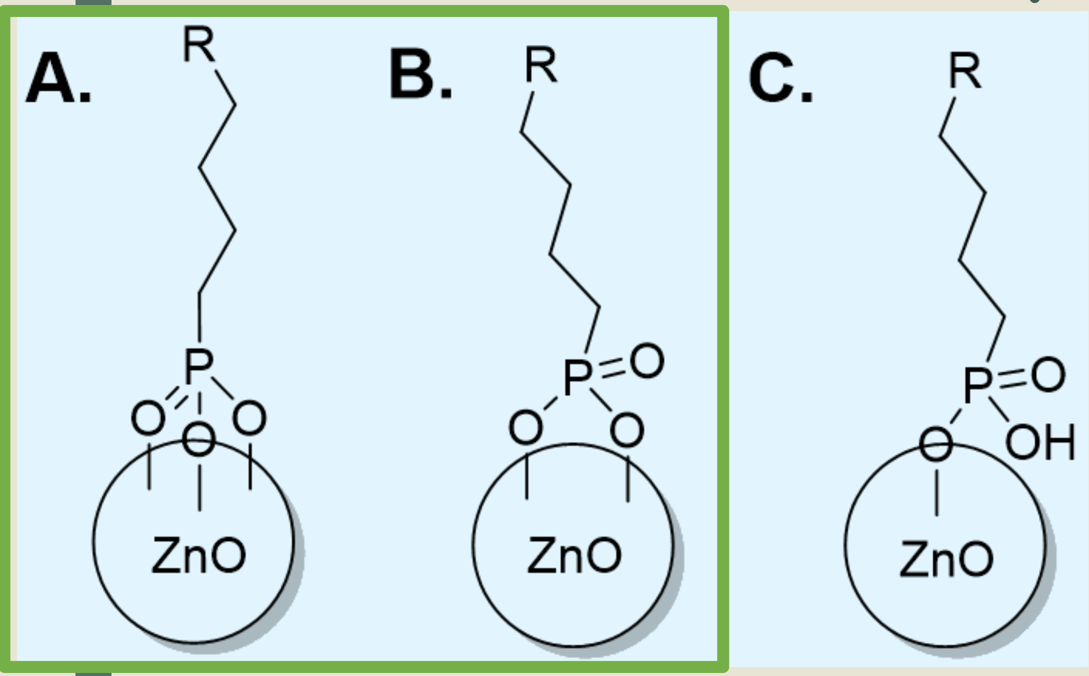
0.01 mmol ZnO-ODPA

0.045 mmol ZnO-ODPA



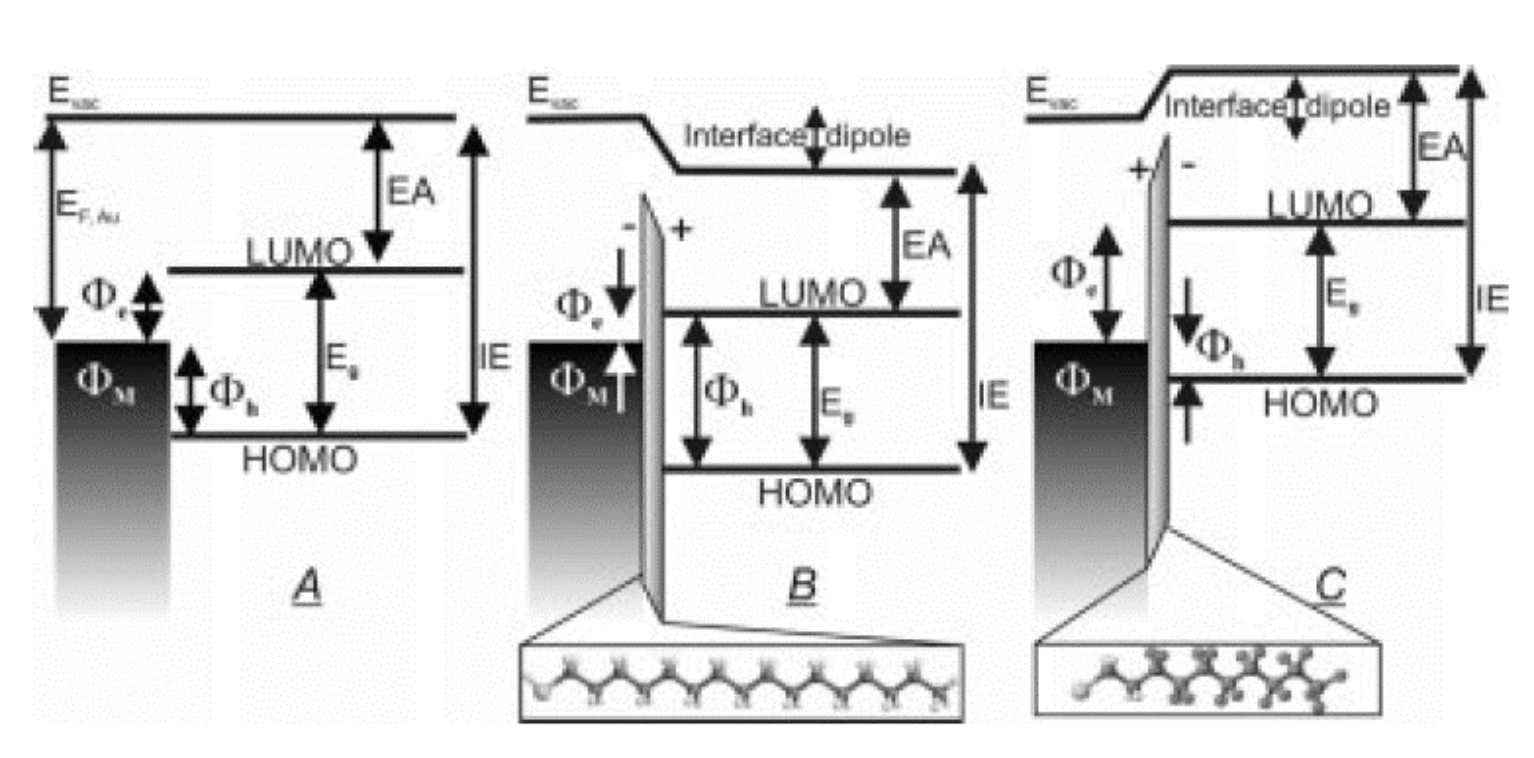
100 µm

^{31}P SS-NMR: Bonding



- ^{31}P chemical shifts of headgroups reflect nature of surface attachment
  - *Control: 31 ppm*
  - *Attached: multiple broad peaks from 22-35.9 ppm*
  - *Shift: chemical bond between acid monolayer and nanoparticle surface*
    - *Upfield shift is associated with the chemically bonded phosphonic acid film with the ZnO surfaces*
    - 0.01 and 0.02 mmmol- tridentate preference
  - *Broadening: distribution of binding sites*
  - *Increased number of peaks: different types of surface bonds and binding sites on ZnO surface*

Energy-level diagrams of Metal/Organic Interfaces with metal work functions



Adv. Mater, **2005**, 17, (5), 621-625

Ultraviolet Photoelectron Spectroscopy (UPS)

Modifications	Work function ($\Phi \pm 0.1$ eV)
ZnO	4.4
0.010 mmol ZnO – ODPA	3.3
0.020 mmol ZnO – ODPA	3.9
0.045 mmol ZnO – ODPA	4.0
0.090 mmol ZnO – ODPA	4.4
0.020 mmol ZnO – COOH-PA	5.4
0.045 mmol ZnO – COOH-PA	5.6
0.020 mmol ZnO – Di-PA	5.6
0.045 mmol ZnO – Di-PA	5.9

- Hole-injection and electron-injection barriers are linearly dependent on an electrode's work function.
- Surface potential is directly proportional to the effective work function
- Organic molecules anchored on metal or oxide surfaces can produce a permanent dipole moment at the interface
- Methyl-terminated modified samples work function ranges from 3.4 to 5.4 eV depending of surface coverage and film thickness

Conclusions

- Confirmation and characterization via IR, SEM, PXRD, and SS-NMR
  - *Organic acids SAMs formed strongly-bound, mostly ordered monolayers that remained attach after various stability tests*
  - *Thin films were adsorbed on the surfaces through the phosphonate group*
- The photoresponsivity is highly desired for photovoltaic applications such as in solar cells
- Treatments of the film surface by coating the ZnO nanoparticles was monitored and characterized by calculating work function for electronic purposes

Future Work

- Modification of ZnO using perfluorinated compounds
- Electrochemical measurements including band gap analysis
- Polymers modifications

Acknowledgements

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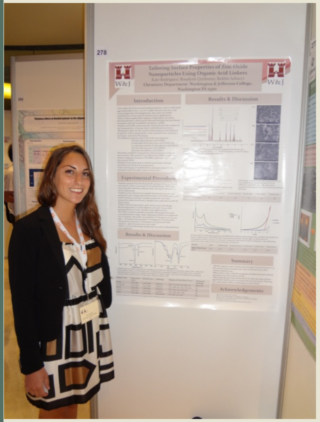

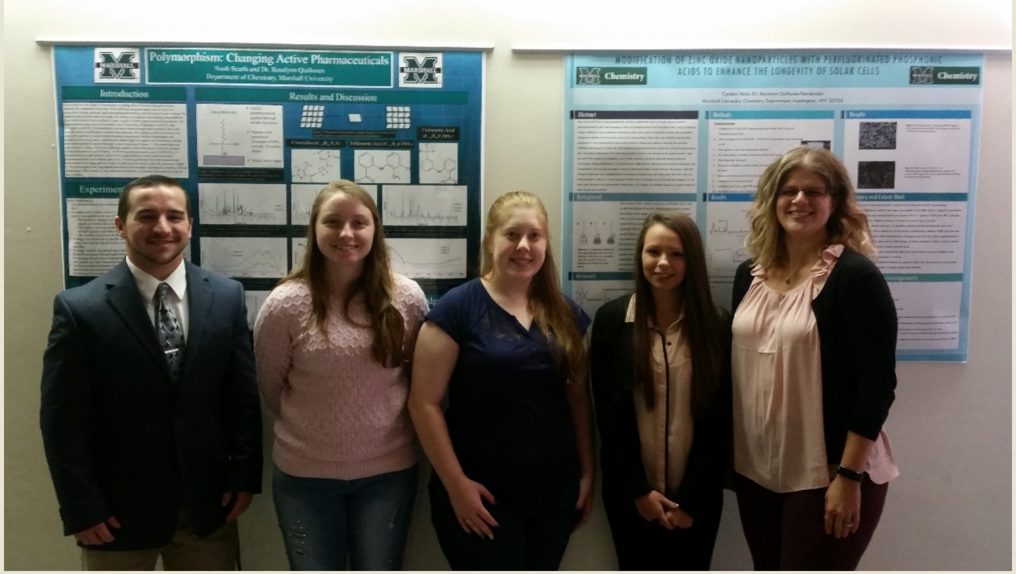

THANK YOU FOR YOUR ATTENTION

Questions??