Team H2 – Final Report
ENMA490

Economical Photocatalytic Water-Splitting

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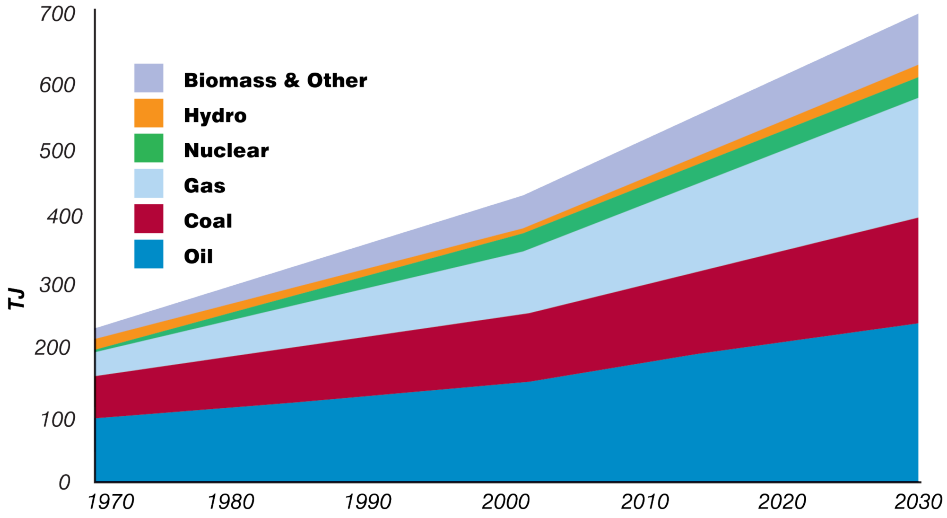
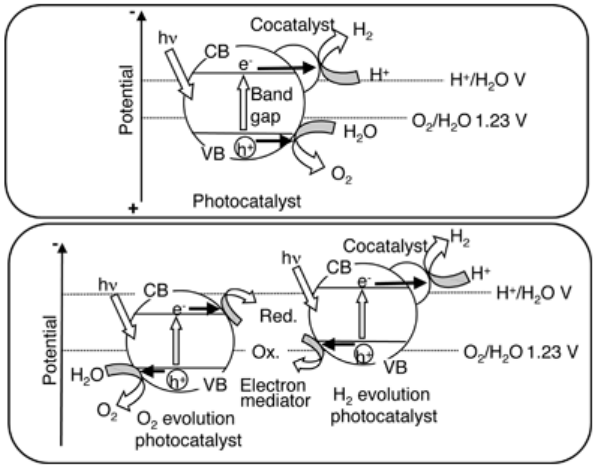
Motivation and Material Science

- Current Energy System Unsustainable
  - Fossil fuels vs. hydrogen



http://www.world-nuclear.org/uploadedImages/org/info/Energy_and_Environment/primaryenergydemand.gif?n=7925

- Nanoparticle Catalysts
- Bandgap Engineering
  - Z-scheme system: photocatalyst (oxidation) and co-catalyst (reduction)

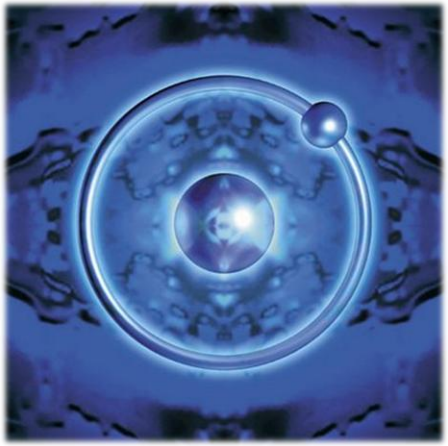


Source: DOI: 10.1039/B800489G

Ethics

BENEFITS

- Fabrication Process
  - Non-toxic
  - Minimal Waste
  - Scalable



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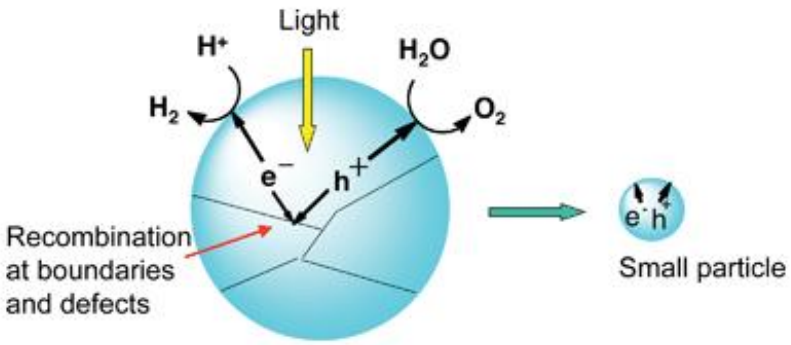
ETHICAL CONCERNS

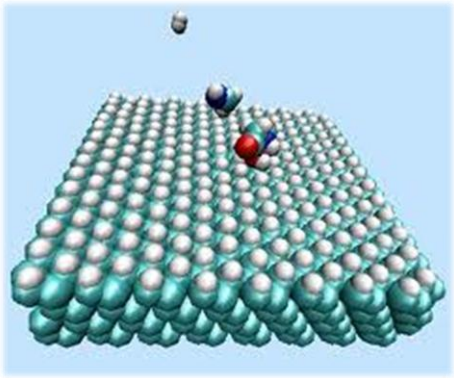
- Potential health dangers of nanoparticles not understood
- Risks of water contamination

http://upload.wikimedia.org/wikipedia/commons/thumb/8/8a/Nrborderborderentrythreecolorsmay05-1-.JPG/300px-Nrborderborderentrythreecolorsmay05-1-.JPG

Intellectual Merit

- Minimization of recombination effects
- Novel combination of catalyst materials
  - $ZnWO_4$ and NiO_x
- NiO formation on a $ZnWO_4$ substrate
  - Kinetic Monte Carlo Simulation





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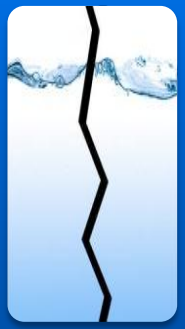
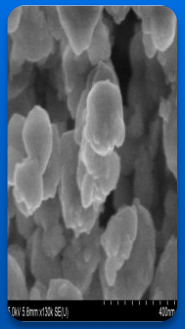
Technical Approach

DESIGN



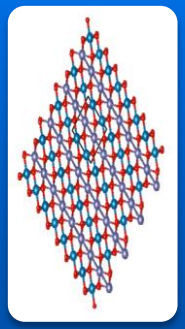
Design Factors

- Size
- Crystallinity
- Surface Area
- Catalyst Material Combination
- Bandgap Engineering



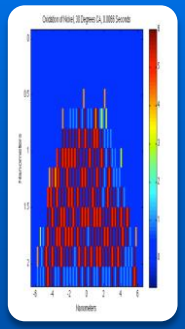
Fabrication and Characterization

SIMULATION



Perform Density Functional Theory (DFT) Calculations

- Determine band edge placements

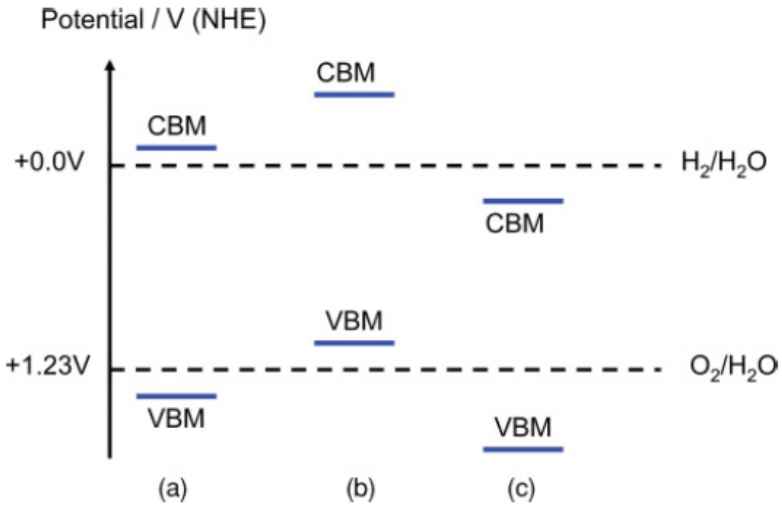


Kinetic Monte Carlo (KMC) Simulations

- Improve Fabrication Conditions

DFT Calculations

- **Band edge placements and band gap of materials correlate directly with water-splitting capability of the material**
  - Minimum band gap for water-splitting w/o voltage: 1.23 eV
  - CBMin < H_2O/H_2 level, VBMax > H_2O/O_2 level
  - Variation as a function of NiO adsorption angle on $ZnWO_4$
- **Vienna Ab Initio Simulation Package (VASP)**
  - Ab initio approach is scalable - suited to handling large data sets

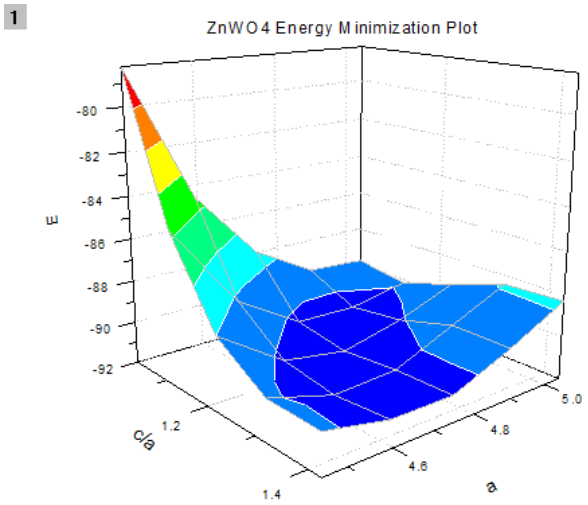


A schematic diagram of possible band level arrangements for water-splitting photocatalysts. a) Favorable band level arrangement b) unfavorable VBM position c) unfavorable CBM position. (Wu 2011).

DFT Calculations

- Original plan for surface calculations had to be scaled down to simpler bulk calculations to determine band gap
- The cells of the materials each had to be relaxed so the minimum energy configuration could be found
  - Lowest energy = most likely configuration

DFT Calculations



Energy minimization plots for $ZnWO_4$ (left) and NiO (right).

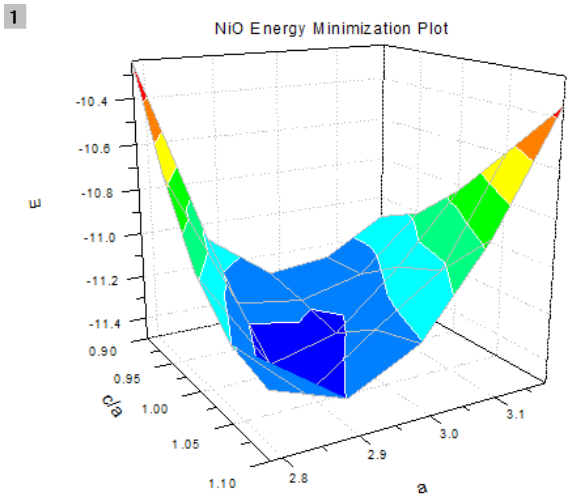
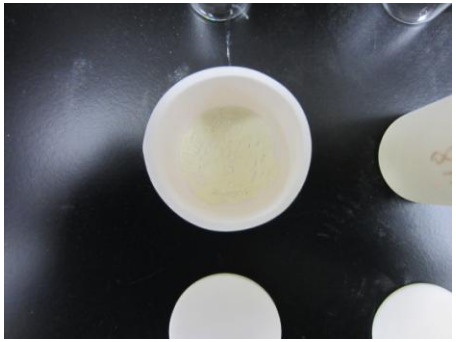


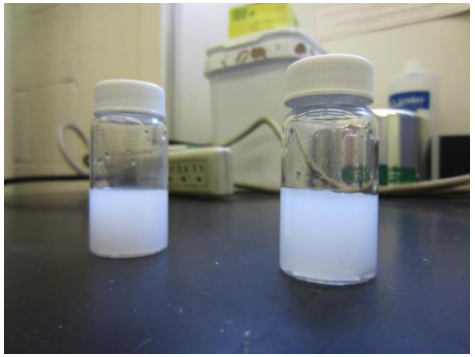
Table I: The calculated and experimental cell parameters for $ZnWO_4$ and NiO.

Material	c/a (Calculated)	c/a (Expt.)	a (Calculated)	a (Expt.)
ZnWO4	1.223379	1.050508	4.744512	4.6925262
NiO	1.05	N/A	2.883756	N/A

Fabrication

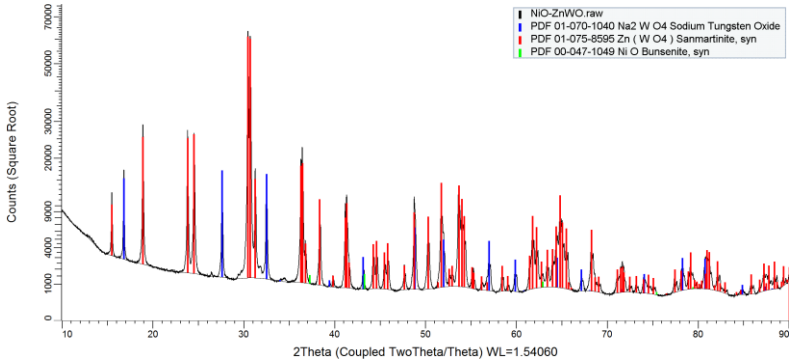
- $ZnWO_4$ synthesis
  - Sonicate $Zn(NO_3)_2$ and $NaWO_4$ mixture
  - Filter and wash mixture
  - Calcine for 4 hours at 500 °C
- Ni Deposition
  - 2 wt% $Ni(NO_3)_2$ is mixed with $ZnWO_4$ particles in DI water
  - Sonicate to aid mixing
  - The mixture is stirred at 80 °C until dry
  - The powder is calcined at 350 °C for 1 hour

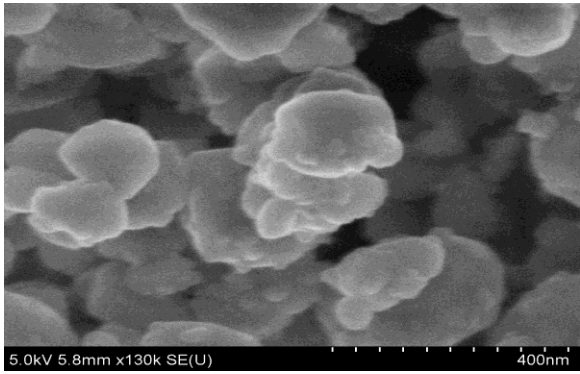


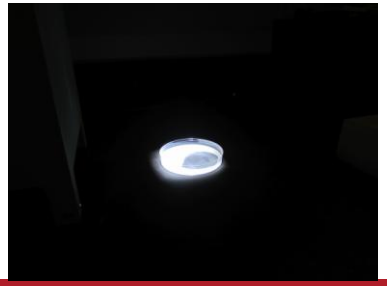


Characterization

- XRD
  - Provided crystal size and composition
  - 89 wt% $ZnWO_4$, 11 wt% Na_2WO_4
  - $ZnWO_4$ avg. crystal size = 157 nm
- SEM
  - Shape, uniformity, and size
  - Spherical and had some agglomeration
- Particle Size Analysis
  - Determines size distribution
  - Average particle size is around 120 nm
    - Unsure about size discrepancy
- Performance
  - Our testing procedure produced inconclusive results
  - Need a gas chromatograph

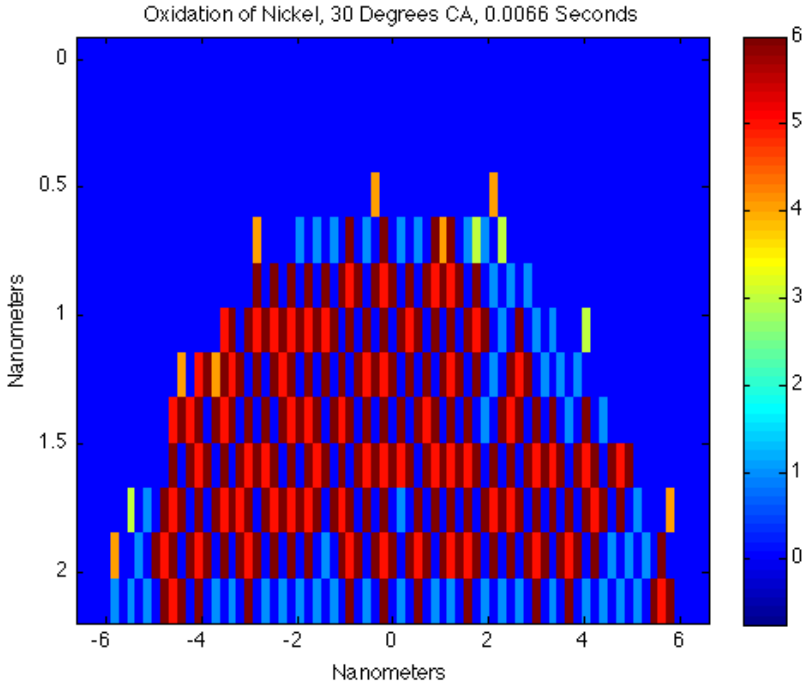






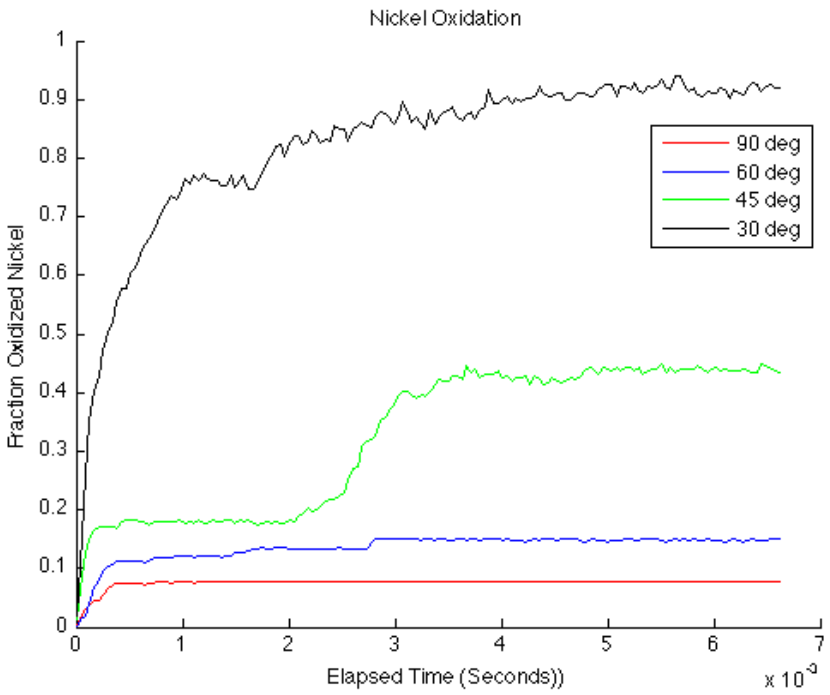
KMC Simulations

- Model oxidation of nickel nanoparticle
  - Diffusion
  - Chemical reactions
- Vary parameters
  - Particle diameter
  - Contact angle
  - Oxidation time
  - Temperature
- Use to adjust fabrication process



Nickel nanoparticle (30 degree contact angle) oxidized for 0.0066 seconds:
(0) Vacancy, (1) FCC nickel, (3) adsorbed molecular oxygen, (4) atomic oxygen, (5) oxygen bonded to nickel, (6) nickel bonded to oxygen.

KMC Simulations



Fraction of initial nickel atoms that were oxidized.

- Oxidation proceeds faster for smaller contact angle
  - 30 degrees: nearly fully oxidized
  - 60/90 degrees: saturates at low oxidation levels
  - 45 degrees: anomalous behavior

Conclusions

Design

- Optimized parameters from literature
- DFT
  - Determined minimum energy lattice parameters
- KMC
  - Preliminary models of nickel oxidation

Fabrication

- Created high crystalline $ZnWO_4$ particles

Results

- Achieved high crystallinity and good composition
- Performance is inconclusive

Future Work

- Refine DFT and KMC Simulations
- Optimize Fabrication Procedure

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