Solar Water Splitting: Photocatalyst Materials Discovery and Systems Development

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DOE Solar H2 Merit Review
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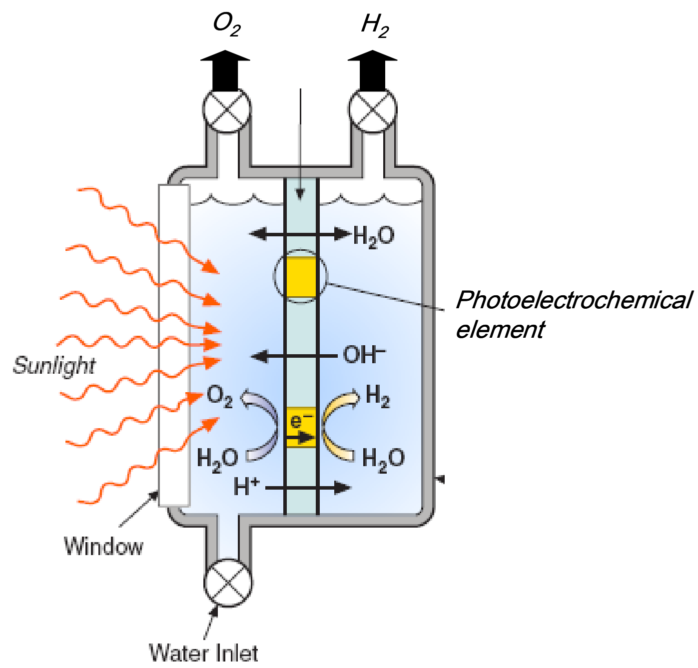
Technical Requirements:

Current
- < 1% efficiency
- 680 $m^2/kg\ H_2$
- \$30.00 /gge (est.)

2015
- 9% efficiency
- 75 $m^2/kg\ H_2$
- \$3.00 /gge (est.)



Efficient photocatalyst (GE lead)

Efficient electron/hole transfer catalysts (Caltech lead)

Robust design; Low-cost BOS (GE lead)

Task Scope:

- Choose (design if necessary) a suitable photocatalyst material

- CTQ's:
  - Bandgap < 2.2 eV
  - CB/VB must straddle redox potentials of water
  - Bandgap "tunable" by cation/anion doping
  - Stable in acidic or basic environment
  - Efficient electron/hole conductor
  - Compatible with TBD electron/hole transfer catalysts

- Study electrochemical and electronic properties in parallel to determine efficacy of photocatalyst and catalyst

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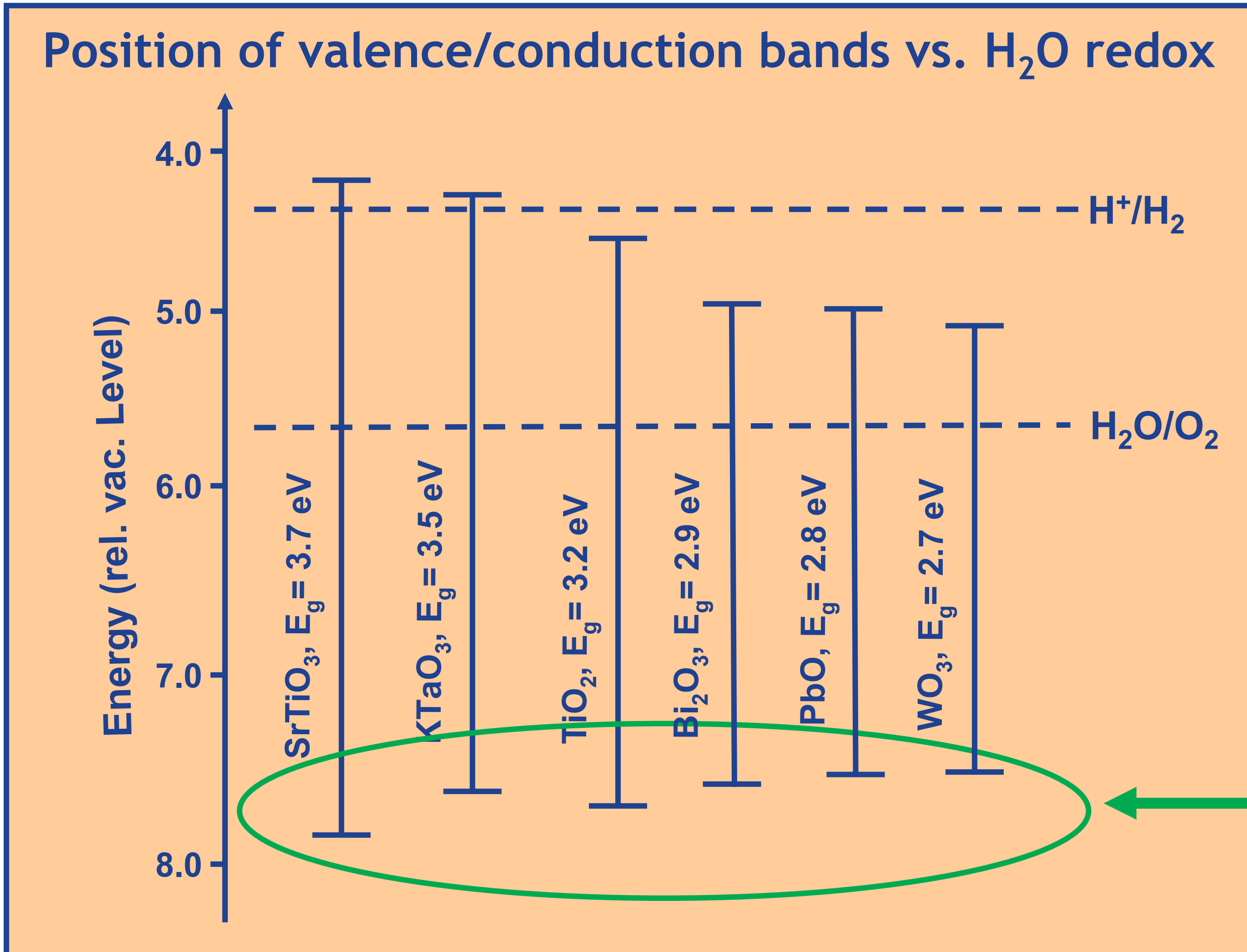
Engineered Band Gap Semiconductors:



Valence band energy level attributed to $O_{2p} \longrightarrow M_{xd}$ transition

Anionic substitution (for oxygen) offers potential…

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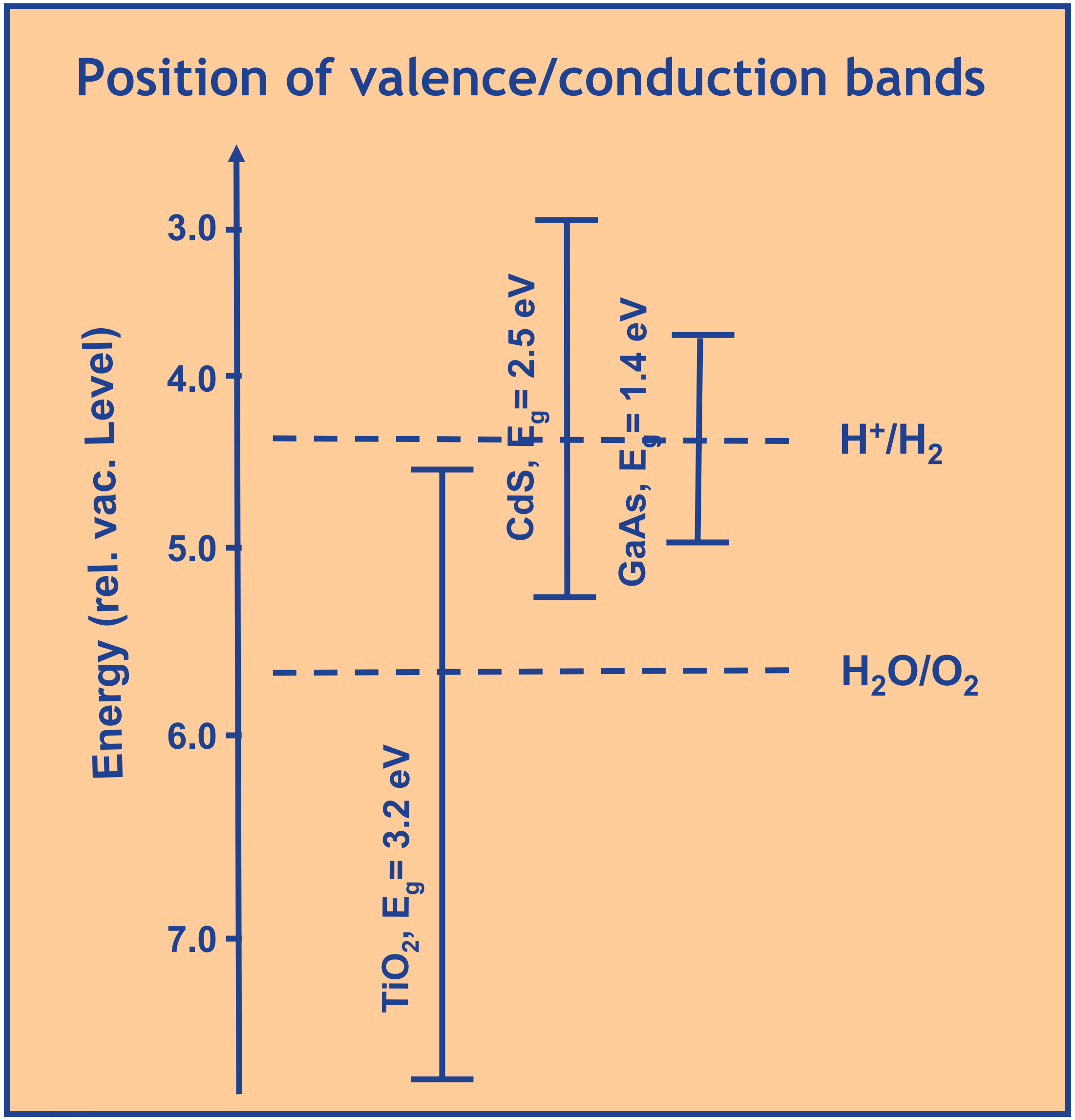
Effect of Anion Electronegativity:



Anion	Electronegativity
O	3.5
N	3.0
C	2.5
S	2.5
As	2.1

Substitution of "softer" anion (lower EN) affects position of VB.

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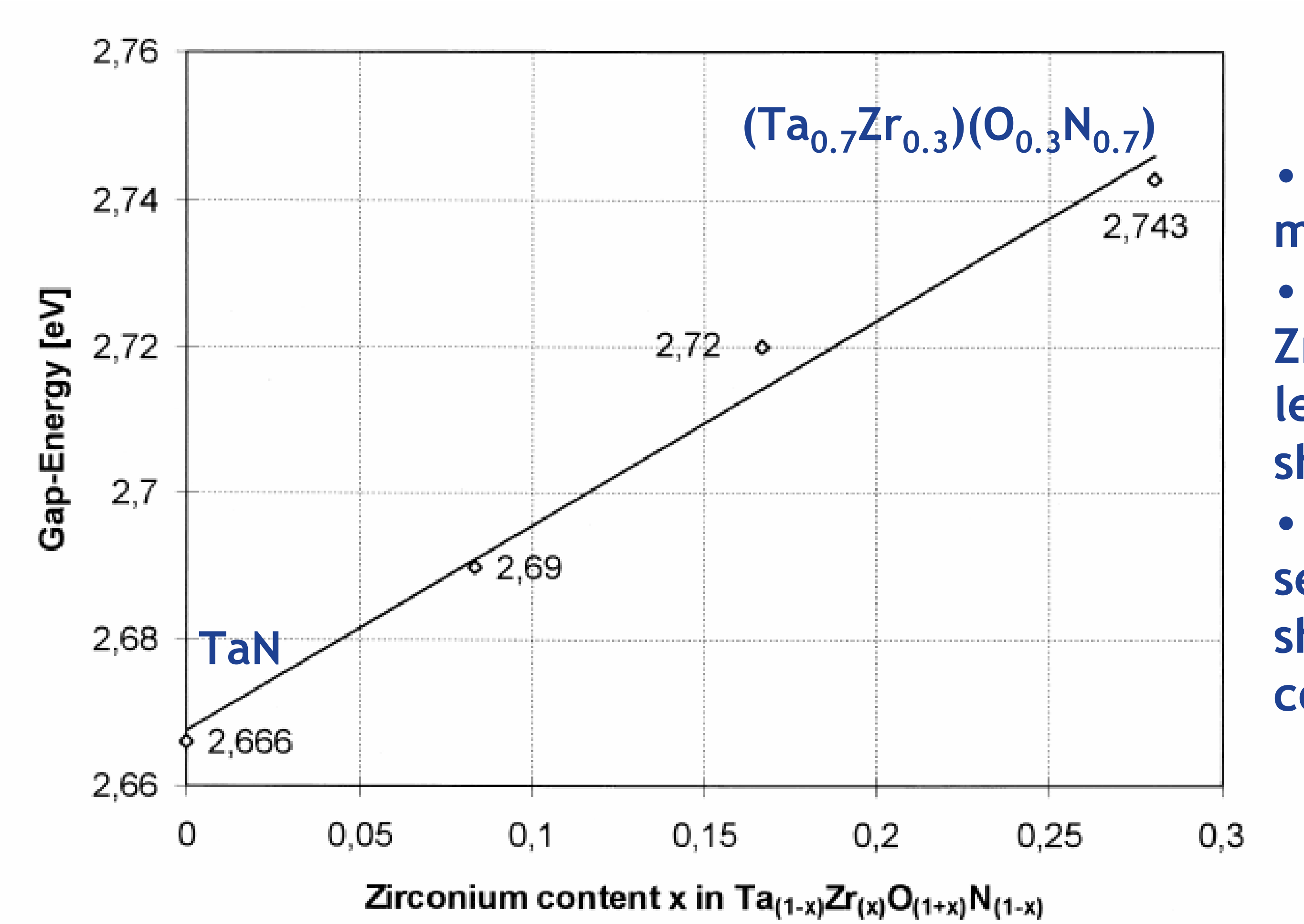
Example 1: Inorganic Pigments

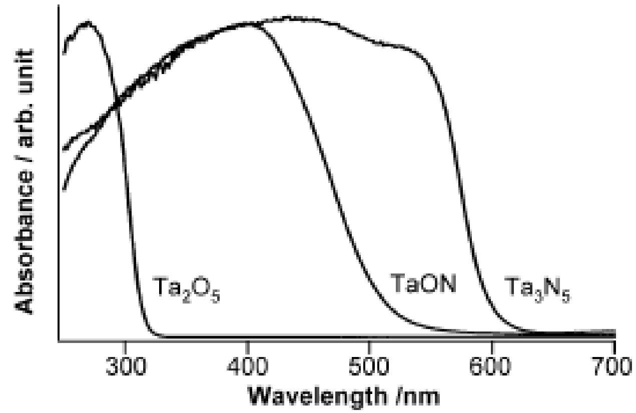


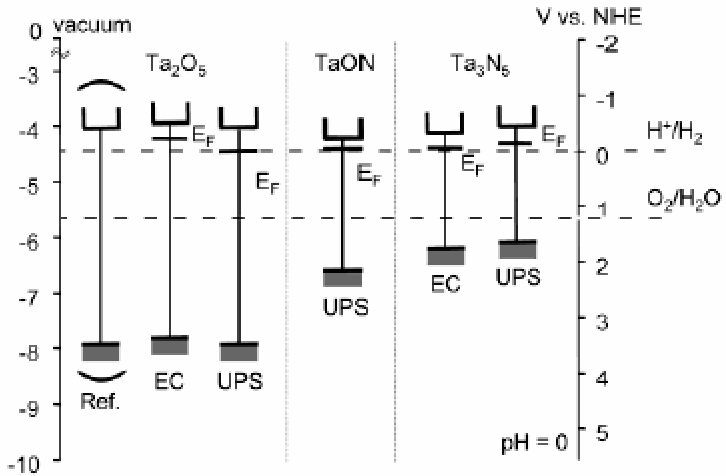
- Oxygen levels mirror Zr
- Substitution of Zr, O w/ > EN leads to bandgap shift.
- TBD is sensitivity of shift, effect on conduction band

Guenther et.al., *MRS Bull.*, **36** (2001) 1399-1405

Background:

- $E_{g,Ta2O5} > E_{g,\ TaON} > E_{g,\ Ta3N5}$
- Difference in E_g occurs primarily in location of VB
- Differences attributable to hybridization of VB by N_{2p} and O_{2p} orbitals, structural effects





J. Phys. Chem. B, Vol. 107, No. 8, 2003

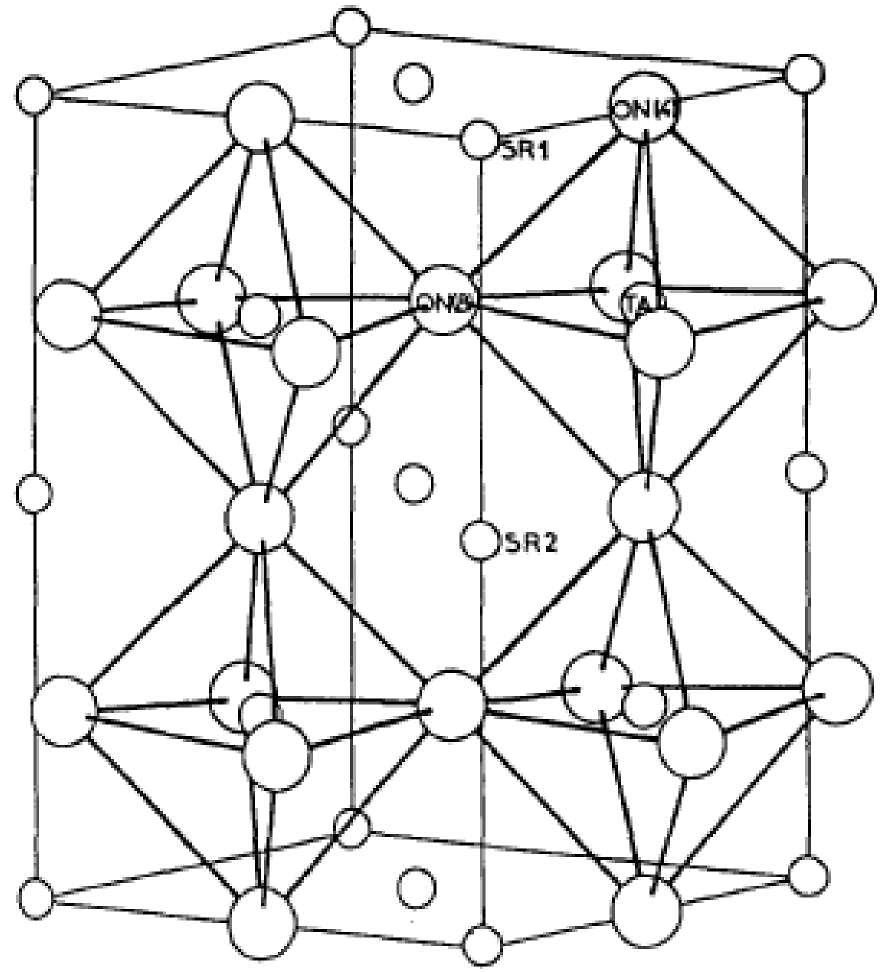
Crystallographic Effects:

(Ca,Sr,Ba)TaO_2N

- Effect of anion/cation doping well documented

- Effect of crystal field on E_g, VB/CB location less understood

- Example: TaON vs. (Ba,Ca,Sr)TaO_2N
    - VB based on hybridized O_{2p} and N_{2p} orbitals
    - CB based on empty Ta_{5d} orbital
    - "disordered oxynitride"; i.e. oxygen and nitrogen interchangable in lattice



Journal of the European Ceramic Society 8 (1991) 197–213

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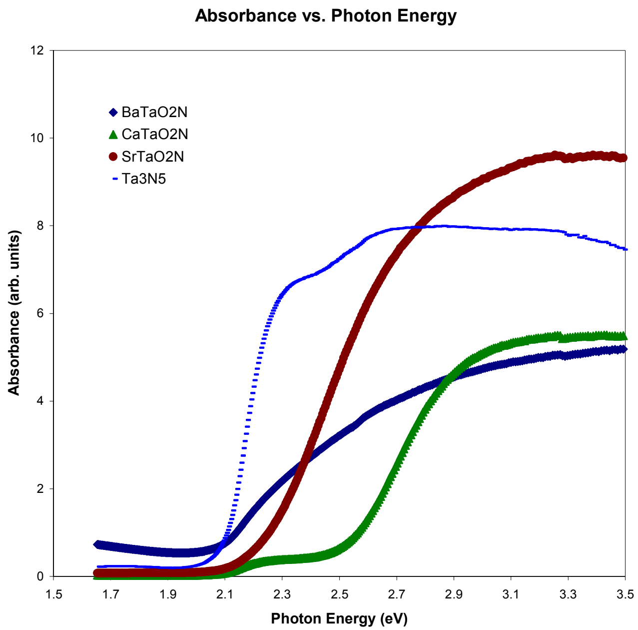
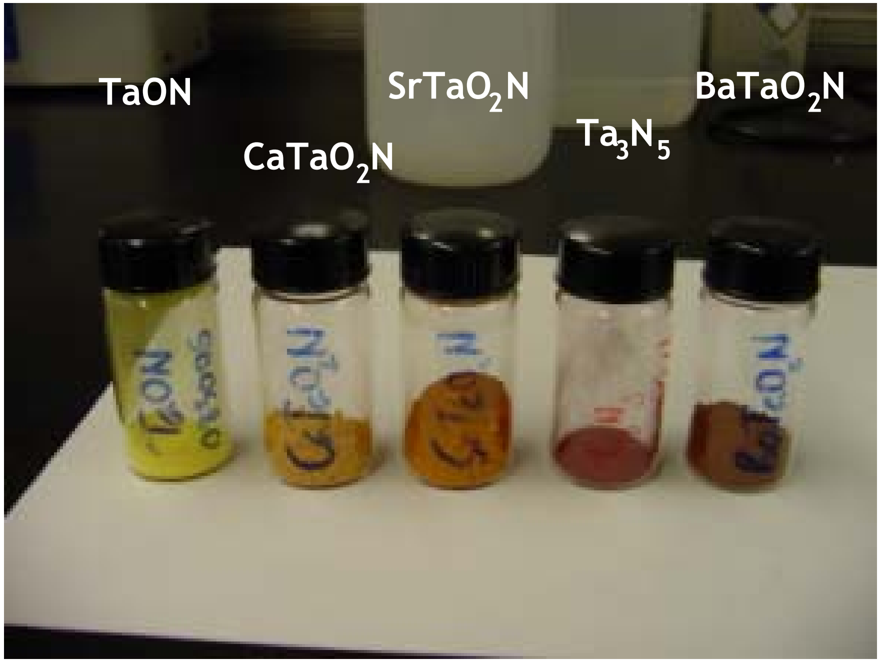
(Sr,Ca,Ba)TaO_2N; Ta_3N_5 syntheses / Characterization:

- Full suite of tantalum nitride and oxynitride materials
- E_g = 2.0 - 2.6 eV
- Patent filed covering $LaTaON_2$ (not shown)





- Solid-state synthesis
- Reacted / nitrided in flowing NH_3:
  - 800 - 900°C
  - 12 - 72h

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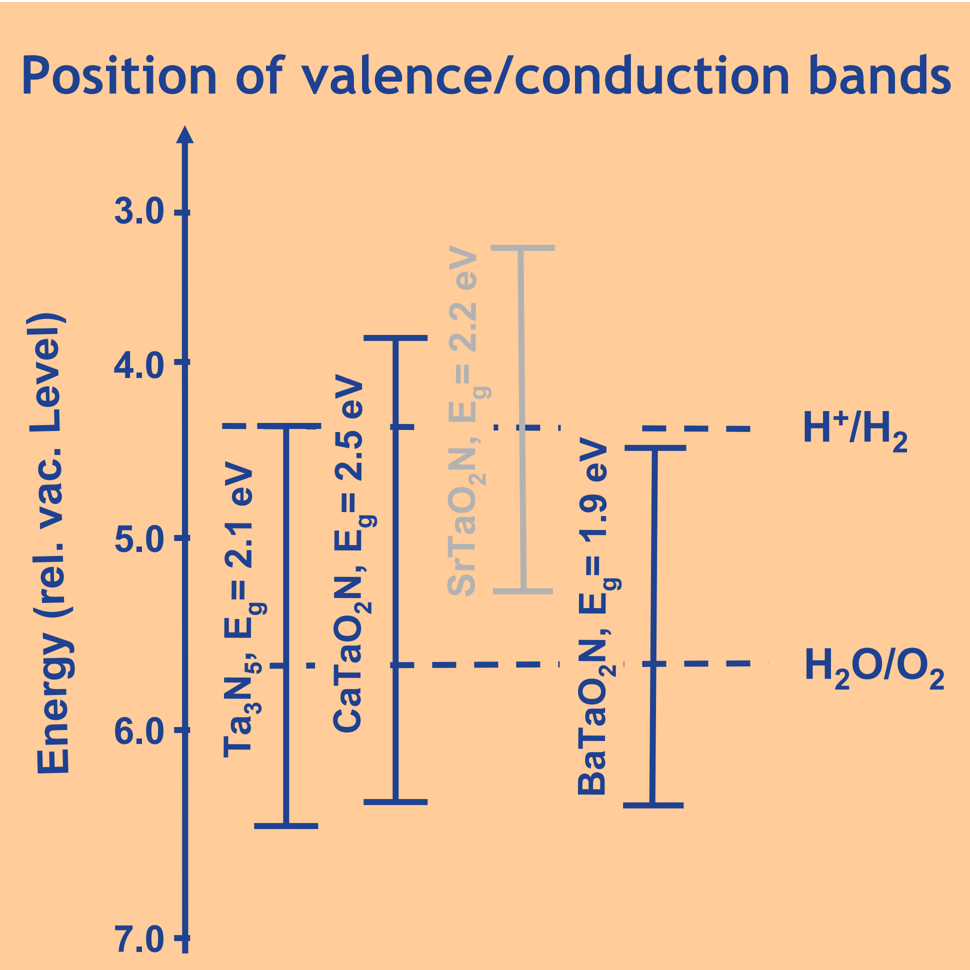
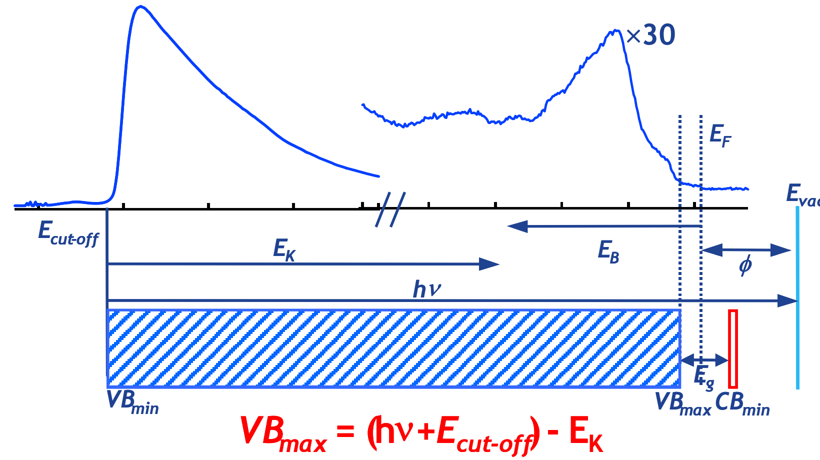
Band Structure Measurements:

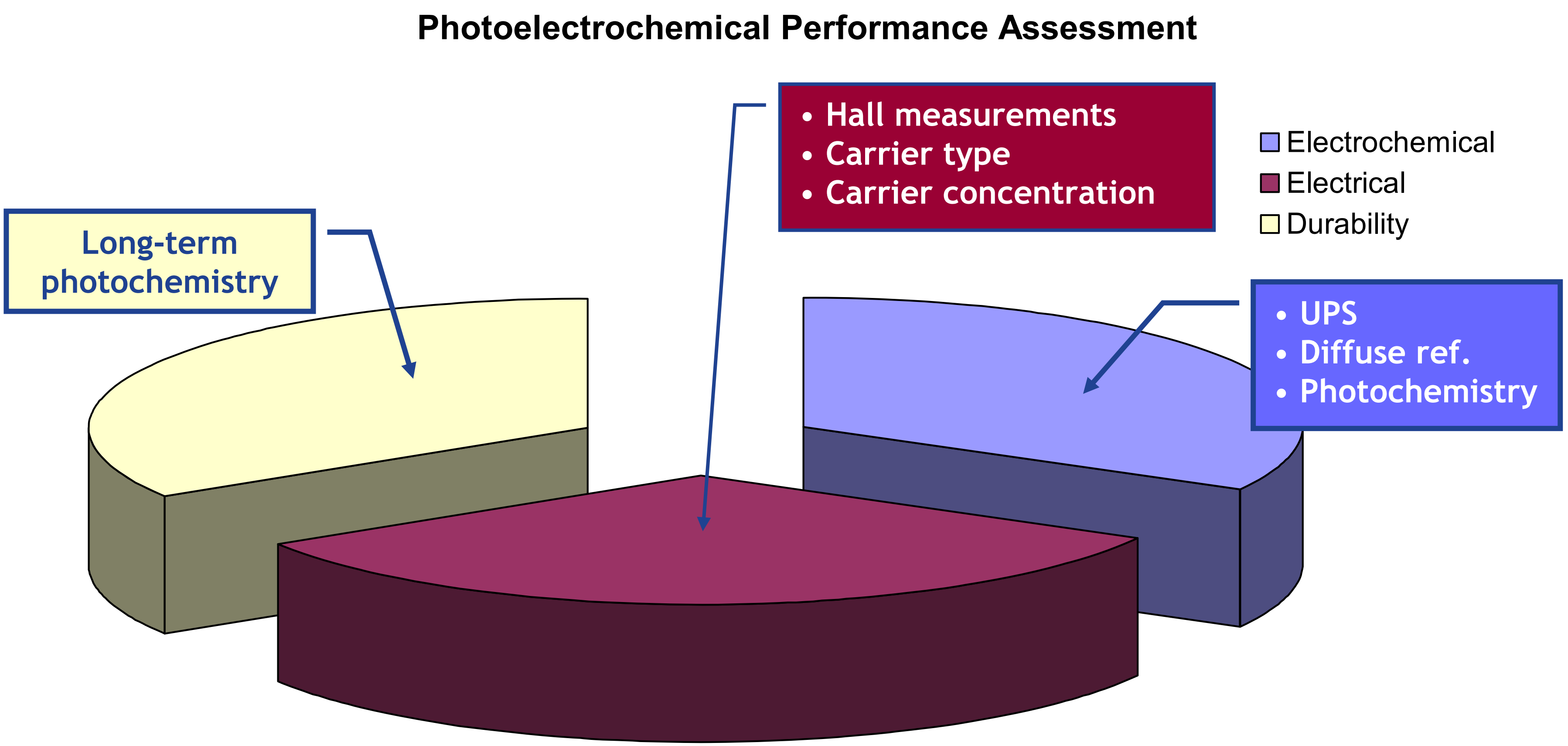




- Ta_3N_5, $CaTaO_2N$ suitable for water splitting
- *(AE)*TaO_2N solid-solution to tune E_g
- $SrTaO_2N$ measurements to be repeated

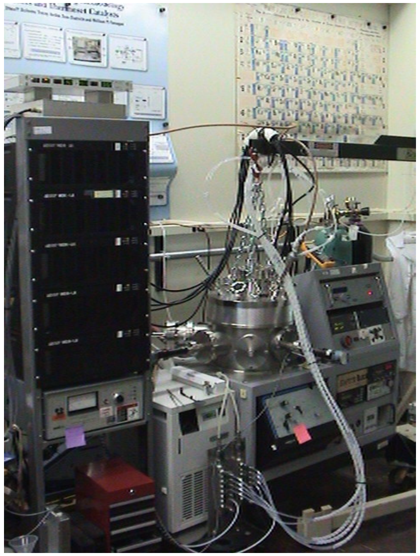
Ta_3N_5 is the "gold-standard"…
Oxynitride perovskites potentially offer better stability…

Performance Assessment:



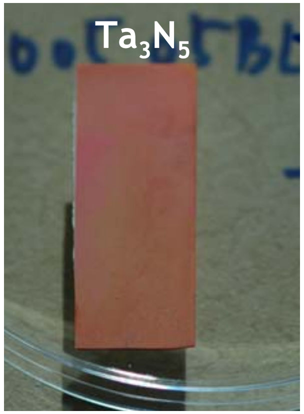
Powders only answer part of the question…
Need bulk samples for electrical characterization…

Thin-Film Synthesis:



Plasma deposition of metallic constituents

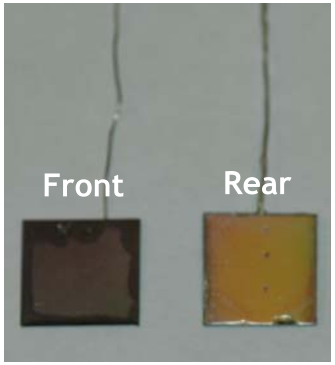
→ Oxidize (700 °C / 4h) air → Nitride (800 °C / 24h) NH_3 →

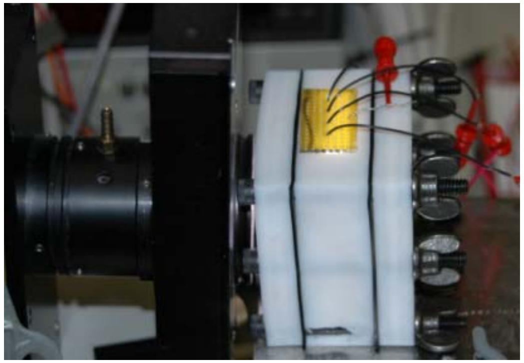


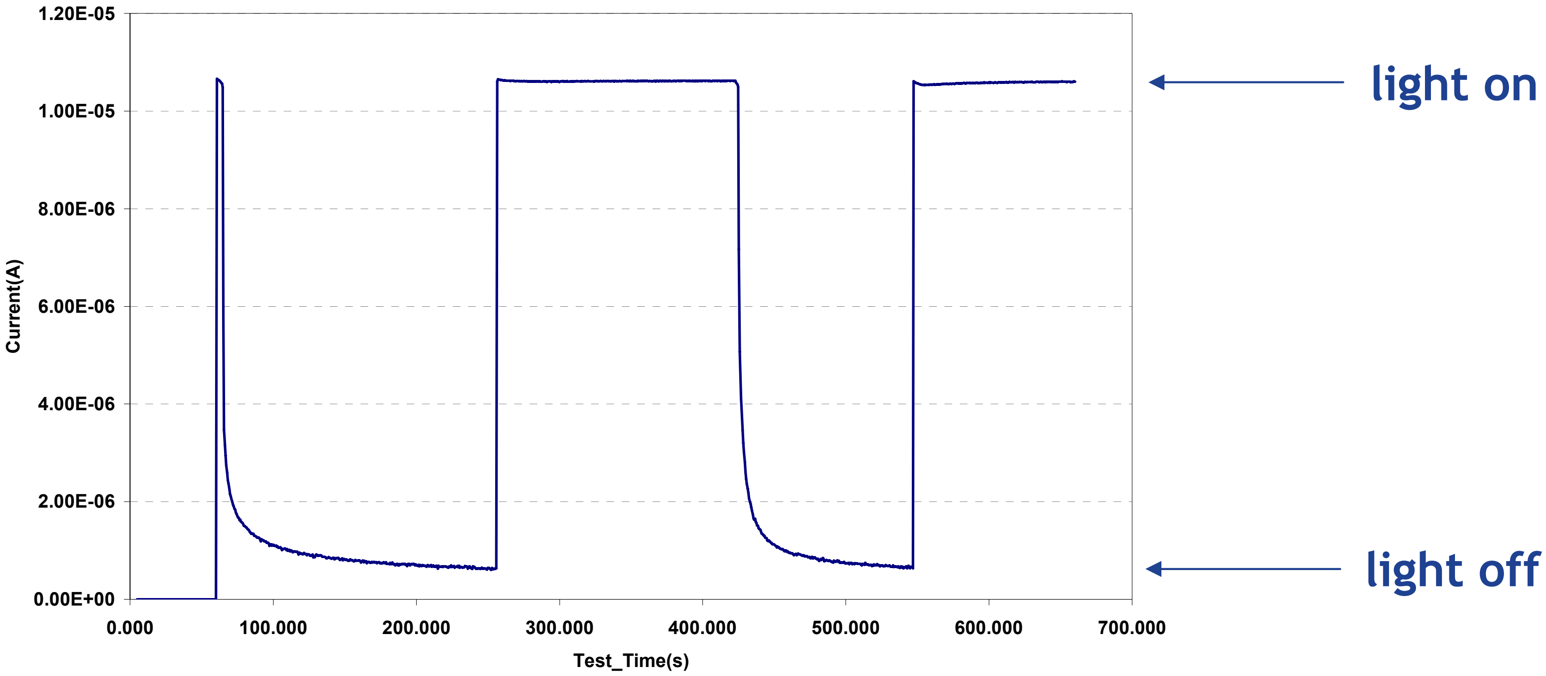
- Base structure: $CaTaO_2N$
- Dopants:
  - Ba
  - Sr
  - La

Enables optimization of electrochemical and electronic properties…
Transition to powders anticipated to be favorable…

Photoelectrochemistry (Ta_3N_5/Ta):







Unassisted photo-splitting of water demonstrated…

Program Status:

- Program Restart 1Q2007 after 1 year idled.
- Critical program deliverables:
    - Photocatalyst → Considerable progress made; High probability of improvements moving forward
    - Transfer catalysts → status unclear; remains significant technical risk
    - BOS → Synergy with electrolysis; Well understood

***What did we learn?* Technology viable; Strong need for renewable H_2 long-term.**

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Future Work

- **Thin Film:**
  - Thin-film production to study photoelectrochemical performance
  - Nitrides, Carbides, etc.
- **Powder optimization:**
  - Optimization of powder morphology for incorporation into membranes
  - Bulk synthesis of powders identified in HTS
  - VB, CB measurements by UPS
- **Membrane development:**
  - Processing optimization
  - Characterization / optimization of surface morphology
  - Membrane-based photoelectrochemical testing

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