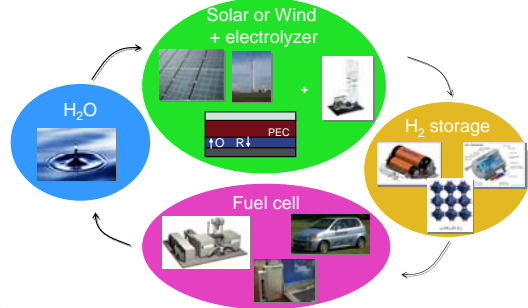


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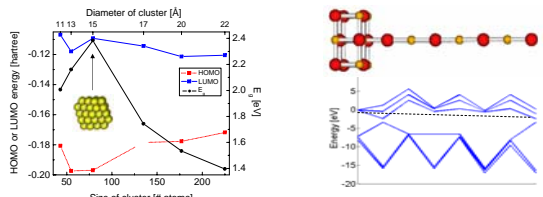
## Photoelectrochemical cells

PECs such as the Dye Sensitized Solar cell represent a promising approach to low-cost clean energy



## Proof of concept

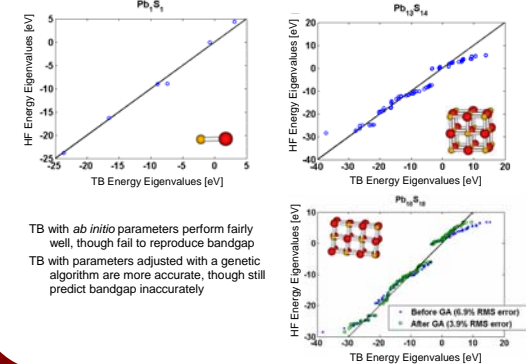
Hartree-Fock calculations of moderate speed and accuracy show a real size and shape effect in Au and PbS clusters



Au, a metal in bulk, is semiconducting at the nanoscale with a bandgap that depends on particle size. Because  $E_g$  increases as the QD diameter shrinks, we must make our light absorbing QD from a metal or low bandgap semiconductor

Solid state physics predicts 1D systems have higher density of states at the conduction band edge than 3D systems. By combining a 1D and 3D system, we can create a built-in E-field that will help drive photogenerated charge carriers towards electrodes

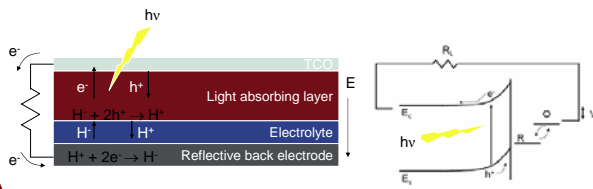
## Tight Binding: calculation results



TB with *ab initio* parameters perform fairly well, though fail to reproduce bandgap  
TB with parameters adjusted with a genetic algorithm are more accurate, though still predict bandgap inaccurately

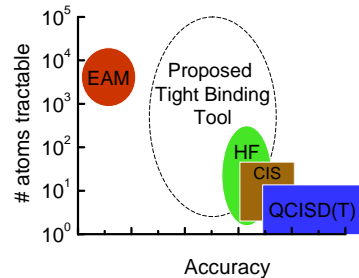
## Device: H+/H- conductor

Simplest redox pair of opposite sign  
Electric field will drive drift current in each direction  
Necessitate thin film electrolyte to minimize recombination



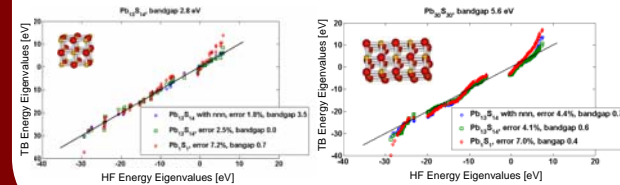
## Tool to calculate bandstructure

Prediction of materials, size, and shape effects crucial to design  
Current tools cannot scale to  $\sim 10^3$  atoms with sufficient accuracy



## Tight Binding: limitations

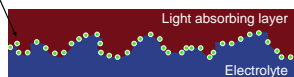
Comparisons to reference calculations of higher accuracy on model systems show TB accuracy limitations  
Inclusion of nnn interactions and better fitting parameters do not always overcome this limitation



## Materials: fabrication and stability

Solid-state electrolyte avoids most longevity issues of DSSCs  
Interface may be nanostructured by bulk heterojunction  
Quantum dots may be sensitizer: continuous control over bandgap, highly optically active, frozen phonon and multiple exciton generation enable efficiency over Schottky limit  
Zeolite electrolyte with small pores will separate  $H^+$  and  $H^-$

QD of metal or low bandgap semiconductor such as PbS

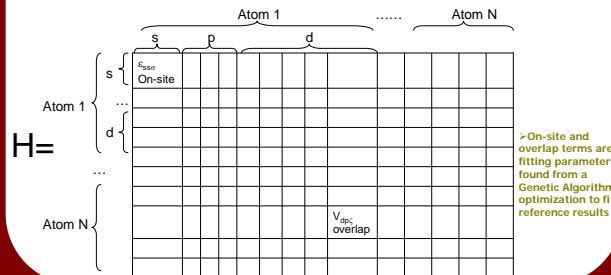


Larger, functionalize basic:  $H^-$   
Smaller, naturally acidic:  $H^+$   
ALD can coat pore interiors to tune pore size and functionalize for acidic/basic environment

## Tight Binding: method

$$\sum_j (\langle \chi_{kl} | H | \chi_{km} \rangle - \epsilon_k \langle \chi_{kl} | \chi_{km} \rangle) = 0 \quad \text{We seek the eigenvalues } \epsilon_k \text{ of the Hamiltonian matrix } H$$

$$H_{ll,mm} = \langle \chi_{kl} | H | \chi_{km} \rangle$$



> On-site and overlap terms are fitting parameters found from a Genetic Algorithm optimization to fit reference results

## Future Work

- Improve accuracy of Tight Binding calculations
- Use TB calculations to evaluate material and geometry design
- Model  $H^-$  stability and diffusion in oxide materials

## Acknowledgements

Dr. Stephen Walch for help in developing basis sets  
Paul Leu for feedback on Tight Binding calculations  
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