Integrated Materials Design: Accelerating the Discovery of New Functional Materials

Sean Smith
Smith team research (UQ/ORNL/UNSW): Computational Nano(bio)science and Engineering

- Titanium dioxide ($\text{TiO}_2$) for photocatalysis
- Catalysis in hydrogen storage
- Functional 1D nano-architectures: electronics & light emission
- Functional 2D materials: membranes, supercapacitors, electronics, photovoltaics, catalysis
- Vector-RNA interactions in gene delivery
- Fluorescent Proteins
- Reaction Dynamics
Center for Nanophase Materials Sciences
Synergistic Science and User Facility

Mission: Enable forefront nanoscience within BES, DOE, academia and industry

- Provide state-of-the-art capabilities for multi-faceted characterization
- Provide unique scientific expertise for synthesis and functional assembly
- Provide advanced nanofabrication capabilities
- Provide leading capabilities in theory, modeling, and simulation
- Enabling neutron sciences at ORNL

Enabling a vibrant user science program
Driving a powerful in-house science program
But, where to beyond the NNI?

- **Mesoscale science**
- **Materials Genome**
Computing power will be a major force towards accelerated discovery of new materials
FUTURE MATERIALS DISCOVERY: A powerfully integrated materials design loop

Function, Applications, Technologies

Theory & Computation

Synthesis

Fabrication

Characterization

Leadership Computing

Neutrons

E-Beam

X-Ray

High throughput computing + Small volume material synthesis + High throughput characterization = Rapid Discovery of New Functional Materials
Computational Modelling has several major contributions to make here:

- Pre-screening of promising materials for different applications.
- Aiding development of synthetic routes to make new materials.
- Helping to interpret and understand experimental results.
- Making “blue sky” predictions of new materials and properties.
- Helping understand molecular mechanisms where it is complex to figure it out any other way.
Many applications for TiO$_2$ (nano)particles:
- photocatalysis for water purification or water splitting
- solar energy cells

Anatase TiO$_2$ single crystals with very large proportion of highly reactive surfaces – almost a contradiction of terms!!

Synthesis and doping strategies to intrinsically modify TiO$_2$ spectral properties for visible light absorption (no dyes!).
New Synthetic Approaches:

- TiO2 (101) surface is almost exclusively the most stable, meaning that it has a lower surface energy $\gamma$.

- Single crystals are not easy to grow with high purity. The usually inhomogeneous samples are dominated by the 101 facets.

- There have been some hints in the literature that surface chemical modification might be able to alter the relative energetics. Fluorine has been implied in some studies.
Single TiO2 crystals with very large (001) facets!!

A new twist: hydrogenation of TiO2 to produce “black titania”!

Jiang et al., EES, 6, 3007 (2013)
Interpreting and Understanding Self-Assembly on well-defined substrates: Metal-organic CuPc on 2D silicon versus graphene

Surface-Induced Orientation Control of CuPc Molecules for the Epitaxial Growth of Highly Ordered Organic Crystals on Graphene

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CuPc – stacking controls direction of electron transfer

Copper phthalocyanine (CuPc)

The orientation of pi-stacking that results from epitaxial growth of metal organics such as CuPc on substrates critically impacts the type of electronic application they can be used for.
Silicon or silicon oxide substrate: perpendicular alignment to surface is preferred
DFT + VdW calculations indicate preferred orientation on graphene is parallel to the substrate:

Why the difference?

*Charge transfer* from graphene to CuPc favors the parallel alignment to the surface
Higher temperature process enhances annealing to the lowest energy structure:

- This orientation is superior for organic photovoltaic applications, since the direction of e\(^{-}\) transfer is towards the conducting graphene substrate.
- Can be achieved at least up to 50nm thickness!
Single layer graphene (SLG) gives enhanced orientation properties!

SLG: room temp
Few layer graphene (FLG): room temp
SLG: 130°C
FLG: 130°C

STM: 130°C
SEM: 130°C
SEM: room temp
Hydrogen Storage in Novel Light-Metal Nanostructured Materials

Key Criteria for Mobile Storage:

- High storage capacity: minimum 6.5 wt %
- Desorption Temperature 60-120 °C.
- Reversibility of the thermal absorption and desorption cycle
- Low-toxicity and non-explosive
- Low cost, low weight.
Magnesium Hydride as a Storage Medium

Magnesium hydride, A very promising candidate for H\textsubscript{2} energy carrier in mobile vehicles.

In MgH\textsubscript{2}, the storage capacity of hydrogen is 7.6 wt%.

Lightweight, low cost, easy to make

**Main problems:**

Slow kinetics and very high hydrogenation and dehydrogenation temperature !!
Recent Experimental Findings on Hydrogenation of Mg:

- Ball-milling of Mg nanocomposite materials (start with hydride since it is more brittle).
- Can improve the adsorption kinetics through addition (≤5wt%) of transition metals such as Ti, Fe, V, Pd ...
- Can improve the hydrogen storage capacity (closer to the stoichiometric limit) by addition of carbon graphite or nanotubes.
- Experimental motivation for addition of carbon related largely to physical factors ...
Carbon is seen to increase the absorption capacity.

Transition metals (often in combination) enhance kinetics.
H$_2$ Dissociation Barrier on Mg(0001) Surface – GGA(PBE) with PAW

Activation Barrier = 1.05 eV
The formation energy of Ti@Mg(0001) surface involves the creation of a Mg vacancy on Mg(0001) surface in the first step and the vacancy is then occupied by a Ti atom.

\[ E_{ad}^{sub} = E_{Ti/Mg(0001)-sub} + E_{Mg} - E_{Ti-atom} - E_{Mg(0001)} \]

\[ E_{ad}^{sub} = -4.09 \text{ eV} \]

There are strong interactions between the molecular orbital of H2 with d metal states of Ti. (Charge is donated from H2 s-orbital to d-states, accompanied by a back-donation from the d-states to the H2 anti-bonding state)
Barrier Calculation for Ti-incorporated Mg(0001) Surface – GGA (PBE) with PAW

Activation Barrier = 0.1034 eV

\[ K_B T(300K) = 0.025 \text{ eV} \]
Pure Mg

Ti incorporated

Further Dressing Ti with Hydrogen ...

Pulling atomic H away from Ti across the Mg surface:

Hydrogen is too strongly bound to Ti – it will not easily diffuse away and so will block the site!
Palladium catalyst – first ab initio validation of the “spill-over” catalytic effect in hydrogen storage
Pd dopant: effective catalysis is a delicate balance of properties!!

The Future: Improved Catalysis for multi-functional performance (absorption, desorption, cycling stability, etc.)

Desorption Remains a Challenge
DNA / RNA delivery is a central problem in biomanufacturing, gene therapy, biopharmaceuticals and drug delivery.

**Cellular delivery:**

- *gene transfection*

  - genetic material: DNA, antisense ODN, ...

- gene therapy

- resistant seeds, ...

- production of various proteins of pharmaceutical value
General Mechanism

LDH

Nanohybridization

Bio-LDH Nanohybrid

Endocytosis

Cytoplasm

Nucleus

8.7 Å

23.9 Å

Choy, J.-H.; Park, J.-S.; Kwak, S.-Y.; Jeong, Y.-J.; Han, Y.-S.
Molecular Crystals and Liquid Crystals Science and Technology, Section A: Molecular Crystals and Liquid Crystals 2000, 341, 425-429
Currently available cellular delivery agents

- Viral delivery
- Non-viral delivery
  - Physical
    - Electroporation
    - Microinjection
    - Biolistics
  - DNA-complex
    - Cationic liposomes
    - Polymers/ dendrimers
    - CaPO₄, inorganic carriers
Biodendrimers as carrier particles

| 3 4+ dendrimer | \[
\begin{align*}
H_2N &\quad C\quad H_2C\quad NH &\quad C\quad H\quad NH &\quad C\quad H\quad +NH_3 \\
&\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 \\
&\quad HN &\quad &\quad NH_3 \\
&\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 \\
&\quad &\quad NH_3 &\quad \quad NH_3 &\quad \quad NH_3 \\
\end{align*}
\] \\
Molecular Weight: 458.60 |
| 4 8+ dendrimer | \[
\begin{align*}
H_2N &\quad C\quad H_2C\quad NH &\quad C\quad H\quad NH &\quad C\quad H\quad +NH_3 \\
&\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 \\
&\quad HN &\quad &\quad NH_3 \\
&\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 &\quad \quad (CH_2)_4 \\
&\quad &\quad NH_3 &\quad \quad NH_3 &\quad \quad NH_3 \\
\end{align*}
\] \\
Molecular Weight: 971.29 |

Dr Harry Parekh (Pharmacy, UQ) and Ouyang Defang
4+ dendrimer: Minor Groove simulation

The example sequence chosen is a 21 base pair siRNA of relevance in clinical studies of cervical cancer.

MD simulations used the AMBER9 software package with the all-atom AMBER99 force field (ff99) for RNA.
4+ dendrimer: 
Major Groove simulation
8+ dendrimer: Minor & Major Groove simulations (final structures)
Dialing up the n/p charge ratio:

0.6:1

1:1
n/p charge ratio 2:1
Structure of solvated dendrimers: Precision deuteration with neutron scattering resolves the debate

Likos et al., 2006: Theory supports dense-core model, but no convincing experimental evidence

Muthukumar et al., 1990: Dense core

de Gennes et al., 1983: Dense shell

Wu et al. (Wei-Ren Chen group), 2011: SANS from selectively deuterated G5 PAMAM dendrimers proves segmental backfolding (dense core) unambiguously (J. Chem. Phys. 135, 144903)

Wei-Ren Chen

Kunlun Hong
What about the water?
Water is structured differently within proximity of a charged dendrimer!

- $\alpha=0$ (neutral); $\alpha=1$ (primary amines protonated); $\alpha=2$ (primary + tertiary amines protonated)
- Pair correlation functions for water do not stabilize to bulk-like behavior until about 5Å outside the exterior of the dendrimer
- Water is less dense and more ordered within / around the charged dendrimer
Modeling Neutron Scattering: Should account for not just the polymer but also the invasive water and cavities!

- To do this correctly requires atomistic molecular dynamics simulations

Dendrimer + counterions  
Dendrimer + Counterions + invasive water  
Dendrimer + Counterions + invasive water + non-bulk water corona
Improved prediction of scattering form factors

- This results in a significantly better fitting to the experimental scattering data
- So, for dendrimers and polymers solvated water is important, and differs from the bulk

Structured water in polyelectrolyte dendrimers: Understanding small angle neutron scattering results through atomistic simulation

Bin Wu,1,2,3 Boutheïna Kerkeni,4 Takeshi Egami,5,6 Changwoo Do,1 Yun Liu,7,8 Yongmei Wang,9 Lionel Porcar,10 Kunlun Hong,2 Sean C. Smith,2 Emily L. Liu,3 Gregory S. Smith,1 and Wei-Ren Chen1,a)
Charged dendrimers swell electrostatically: Core becomes less dense; dendrimer extends further outward

- Invasive water penetrates into the core to fill the extra voids that open up as the dendrimer swells due to electrostatic repulsion
How do we separate out the invasive water from the dendrimer experimentally?

Contrast variation small angle neutron scattering:

- Altering the ratio of $\text{D}_2\text{O}$ to $\text{H}_2\text{O}$ allows to distinguish the invasive water from the actual dendrimer
Electrostatic swelling of the dendrimer is dependent also on the nature of the counterion!
Solvating water adjusts to changes in the dendrimer structure – moves in to fill voids.
Charge of the counterions mediates the electrostatic swelling

Multiple charge on sulphate $\text{SO}_4^{2-}$ coordinates two protinated amine sites – tends to hold the structure together more and reduces the swelling effect.