

Parallel Simulation of Subsurface Fluid Flow

Scientific Achievement

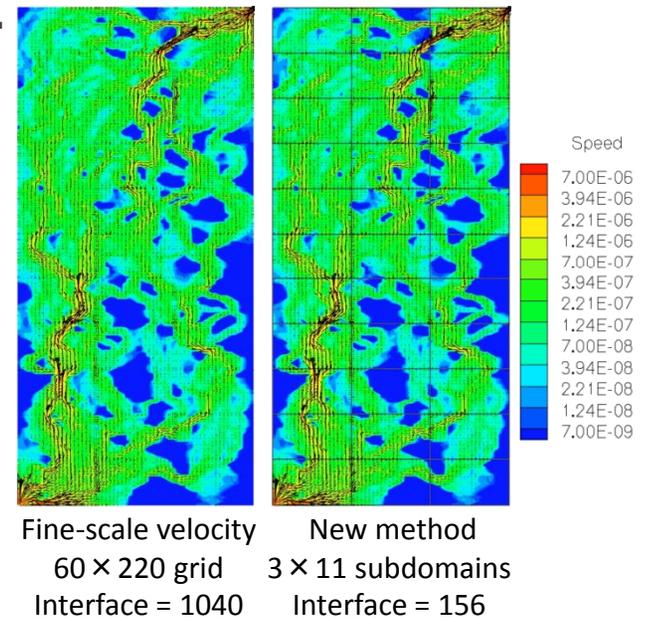
A new mortar domain decomposition method was devised to compute accurate velocities of underground fluids efficiently using massively parallel computers.

Significance and Impact

The sheer size and heterogeneous nature of a subsurface reservoir makes it difficult to compute accurate fluid flow velocities, which are needed to simulate, e.g., the response of a geosystem to injection of CO₂.

Research Details

- Rock heterogeneity, i.e., fine-scale variation in permeability, must be resolved on a fine mesh to compute accurate flow velocities.
- The reservoir is decomposed into subdomains.
 - Each subdomain can be simulated efficiently in parallel.
 - They are tied together through subdomain “mortar” interfaces.
- Homogenization theory predicts fine-scale variations using only a few quantities per interface, tying the subdomains together by to a small and efficiently computed mortar problem.
- Fluid flow can be solved accurately over a huge reservoir volume to a fine resolution efficiently by a massively parallel computer.



T. Arbogast & H. Xiao, *A multiscale mortar mixed space based on homogenization for heterogeneous elliptic problems*, SIAM J. Numer. Anal., 2013.

T. Arbogast, Z. Tao & H. Xiao, *Multiscale mortar mixed methods for heterogeneous elliptic problems*, Contemp. Math., J. Li & H. Yang, eds., Amer. Math. Soc., 2013, Chapter 2.

T. Arbogast, *Mixed multiscale methods for heterogeneous elliptic problems*, in Numerical Analysis of Multiscale Problems, I. G. Graham et al., eds., Springer, 2011, pp. 243-83.



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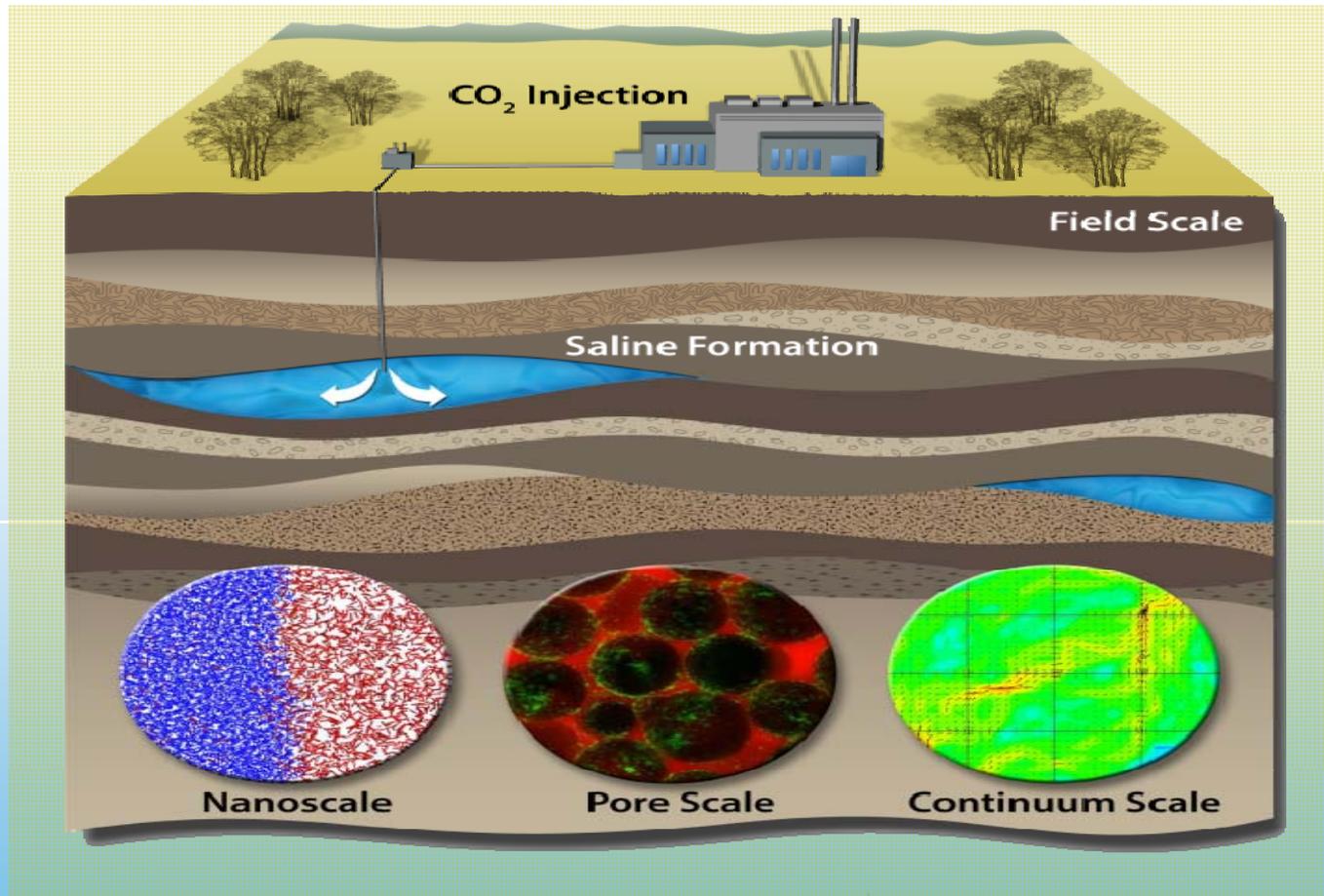
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Sandia
National
Laboratories



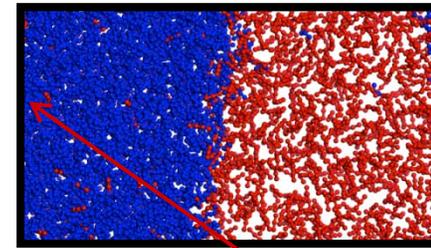
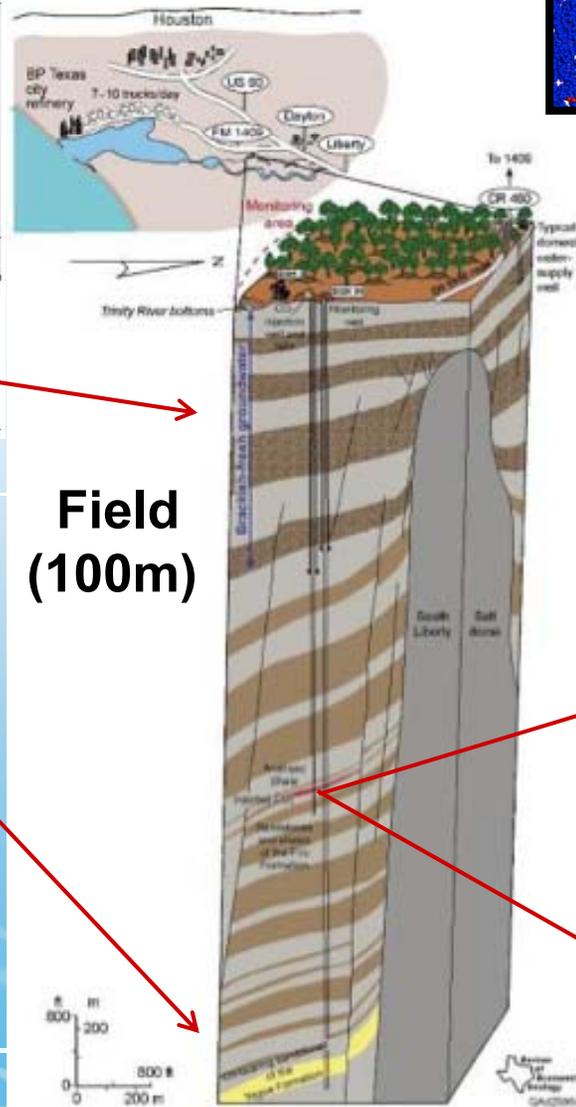
Center for Frontiers of Subsurface Energy Security



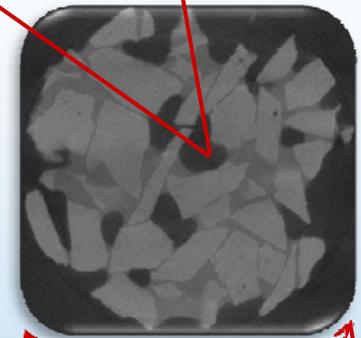
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



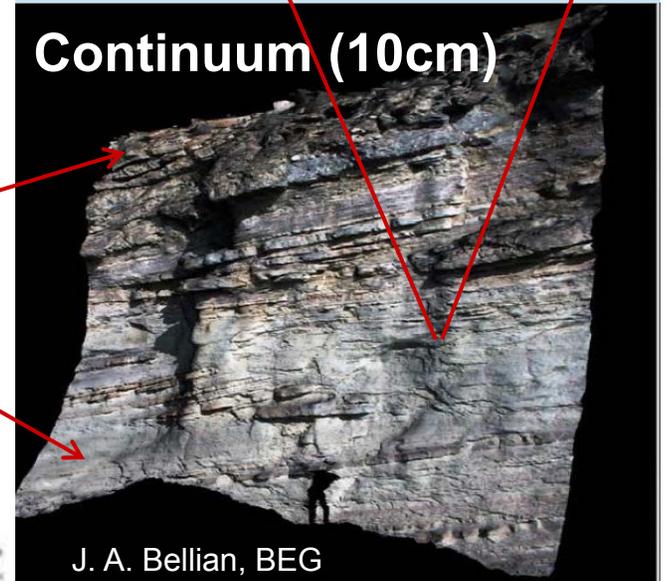
Spanning the Scales in CO₂ Sequestration Simulation



Molecular (1nm)



Pore (10µm)



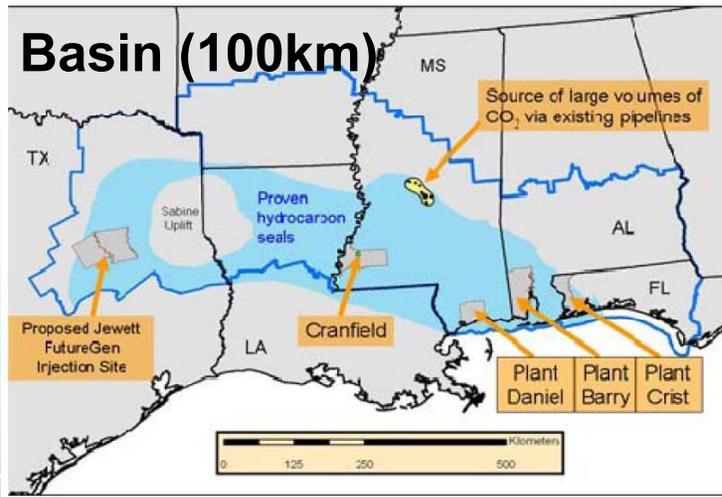
Continuum (10cm)

J. A. Bellian, BEG

Geosystems are **large** and highly **heterogeneous**.

Simulation requires a fine computational mesh and multiscale models.

To simulate geosystem response, we must compute accurate fluid flow velocities.



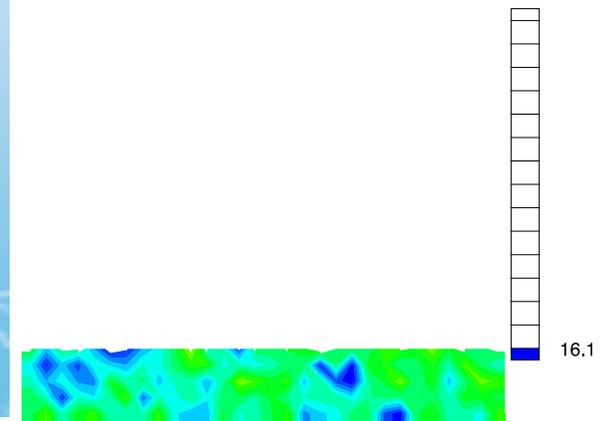
Size & heterogeneity:

- 1m grid spacing?
- Basin: $300\text{km} \times 300\text{km} \times 10^3\text{m}$
= 10^{14} grid-blocks?
- Field: $10\text{km} \times 10\text{km} \times 10^2\text{m} = 10^{10}$
or 10^8 at $10\text{m} \times 10\text{m} \times 1\text{m}$ resolution

Additional computational load:

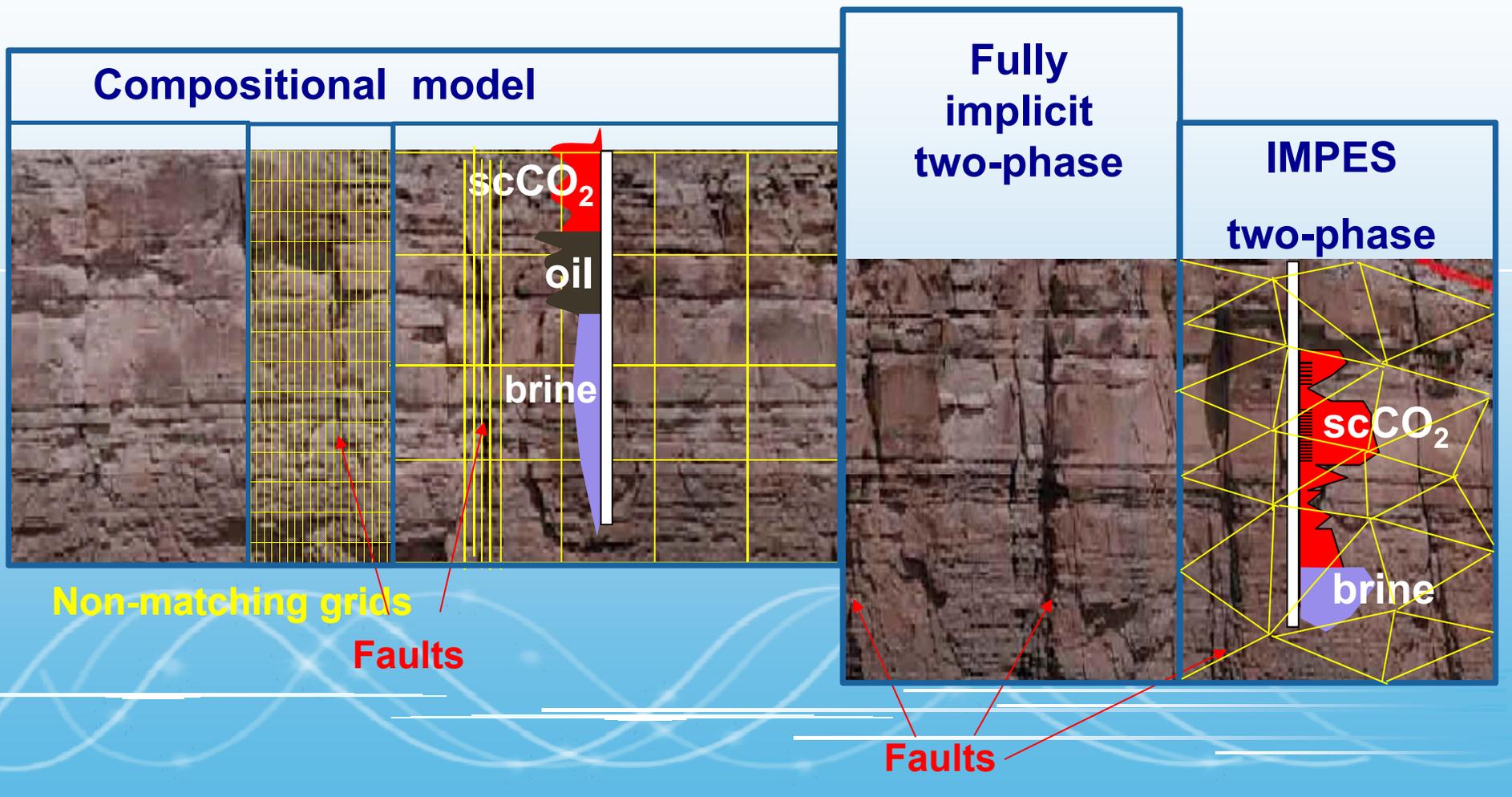
- Multiphase and multicomponent
- Long time simulations (1000 years)
- Uncertainty quantification

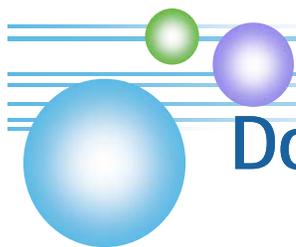
**Need parallel computation
and multiscale techniques!**



The Multiblock Concept

Divide the domain into nonoverlapping subdomains and simulate the relevant processes locally as appropriate. Tie these together through a “mortar” interface.

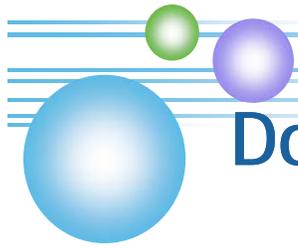




Domain Decomposition Mortar Methods

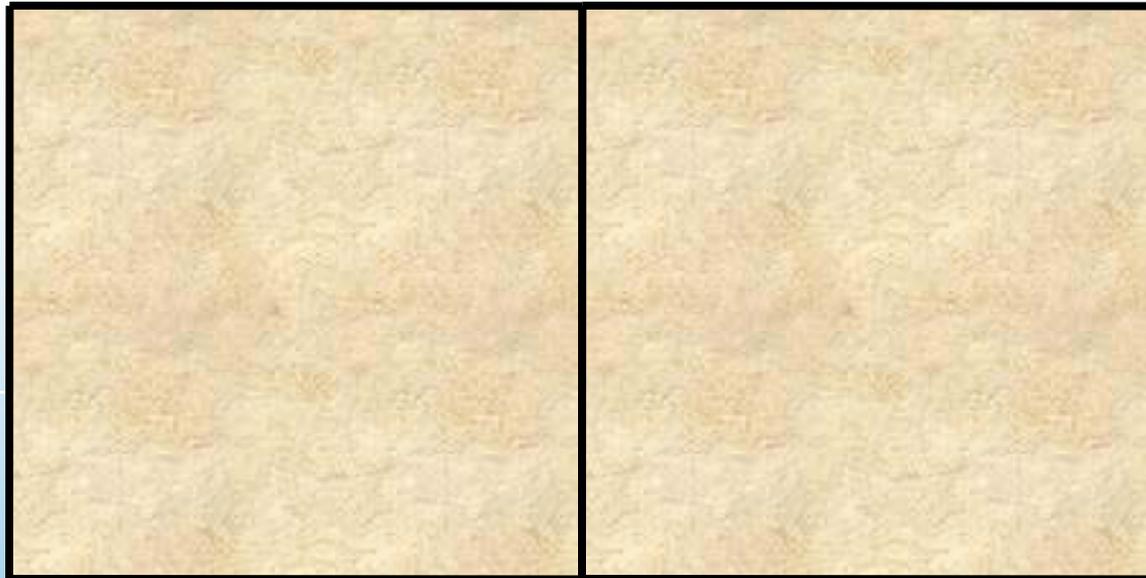
CO₂ Reservoir Domain





Domain Decomposition Mortar Methods

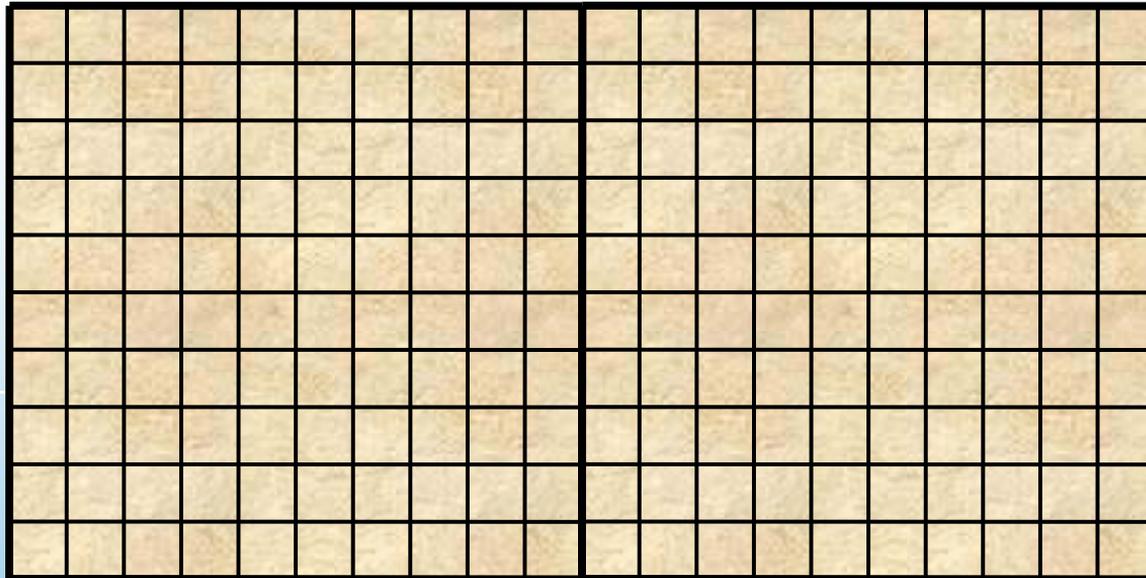
CO₂ Reservoir Domain



Subdomain **blocks** for parallel processing

Domain Decomposition Mortar Methods

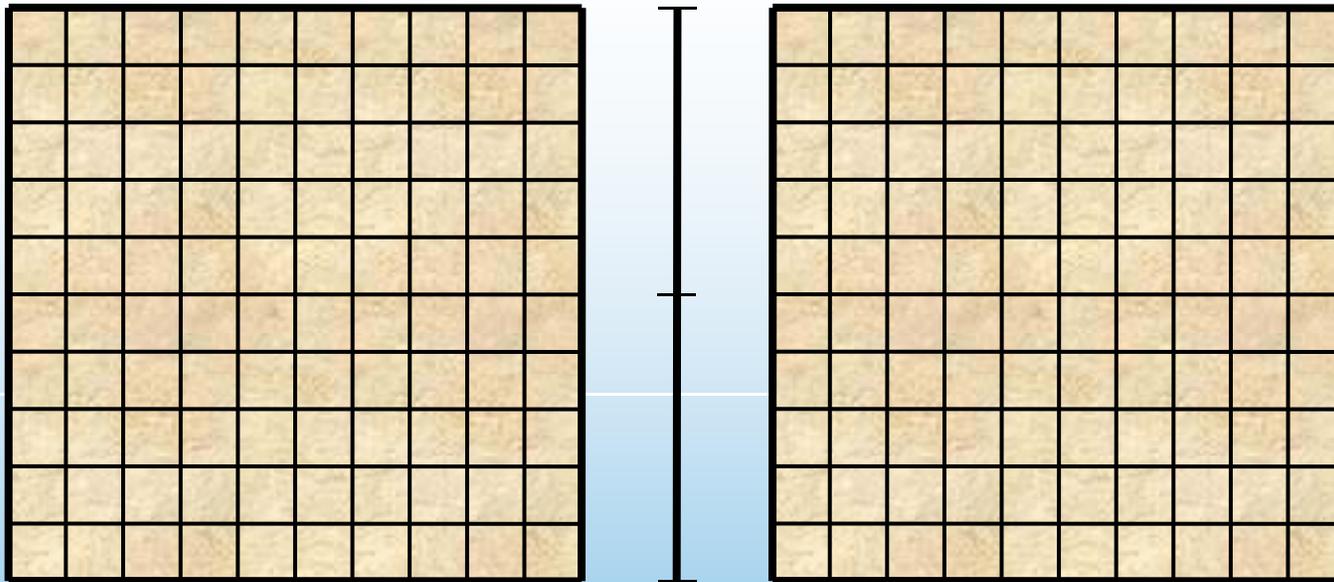
CO₂ Reservoir Domain



Fine grid for resolution: **Many unknowns!**

Domain Decomposition Mortar Methods

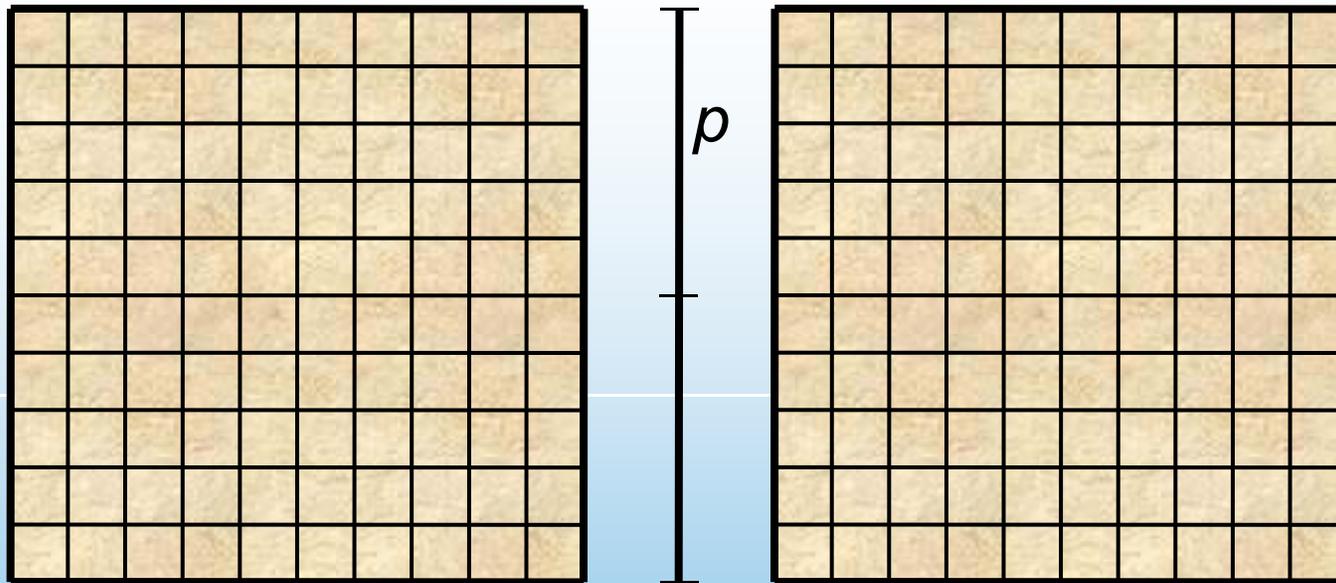
CO₂ Reservoir Domain



Coarse mortar grid: **Few unknowns.**

Domain Decomposition Mortar Methods

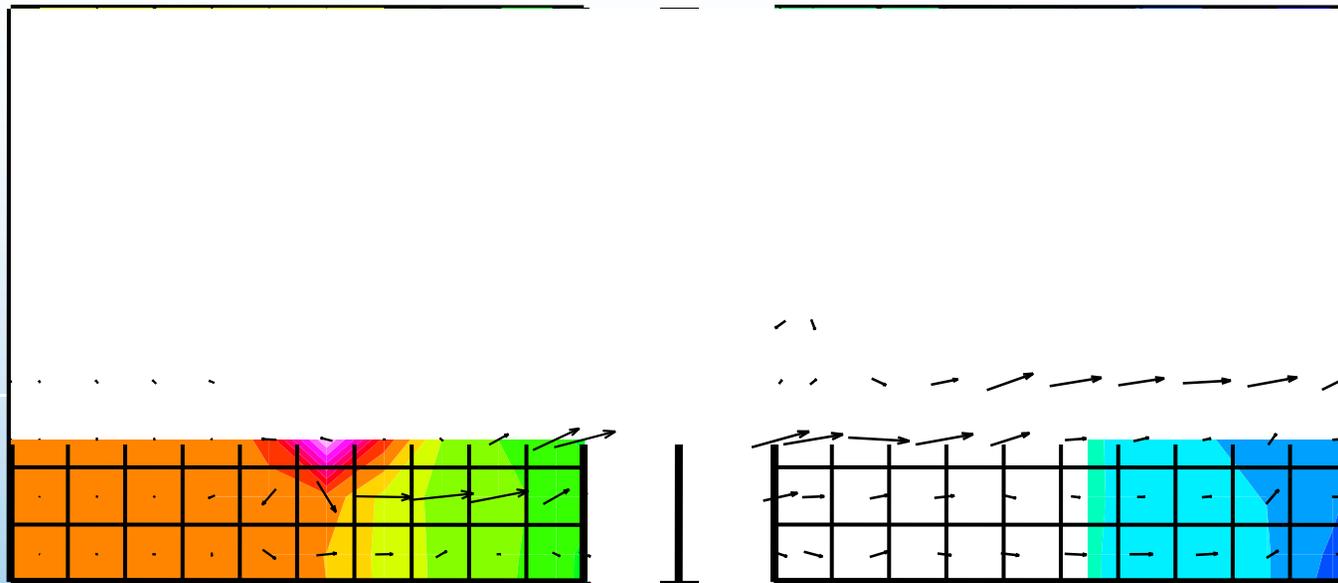
CO₂ Reservoir Domain



Guess mortar pressure p .

Domain Decomposition Mortar Methods

CO₂ Reservoir Domain

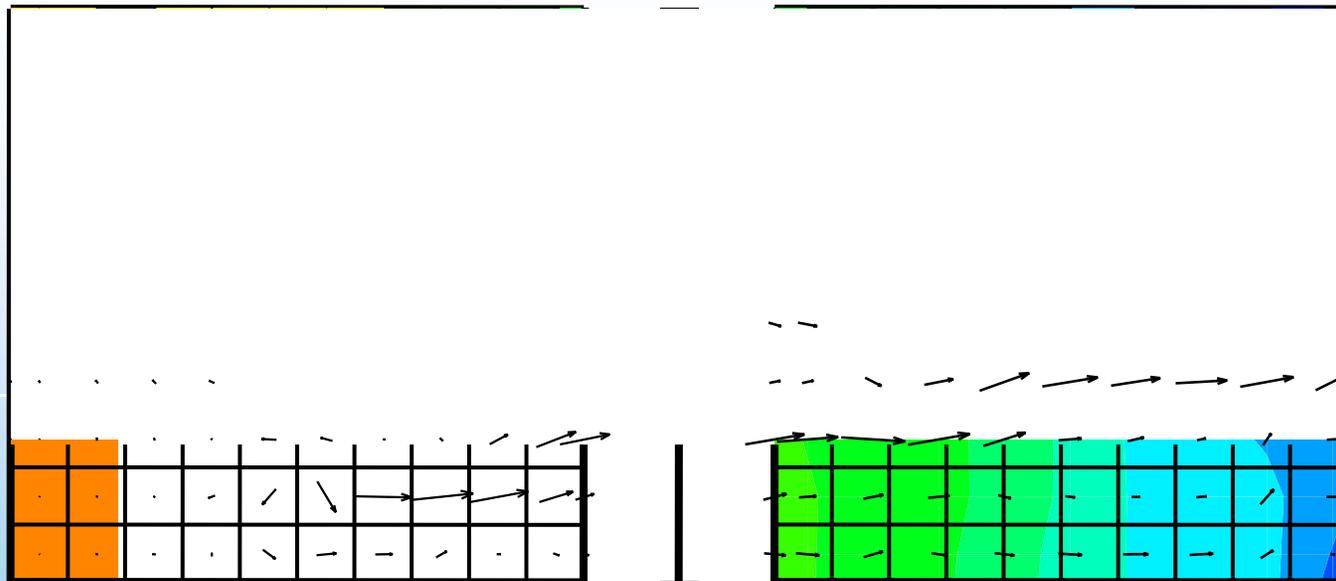


Step 1: Compute the pressure and fluid velocity on each block **efficiently in parallel**.

Based on **velocity mismatch** on interface, update p .
Efficient due to **small size**.

Domain Decomposition Mortar Methods

CO₂ Reservoir Domain

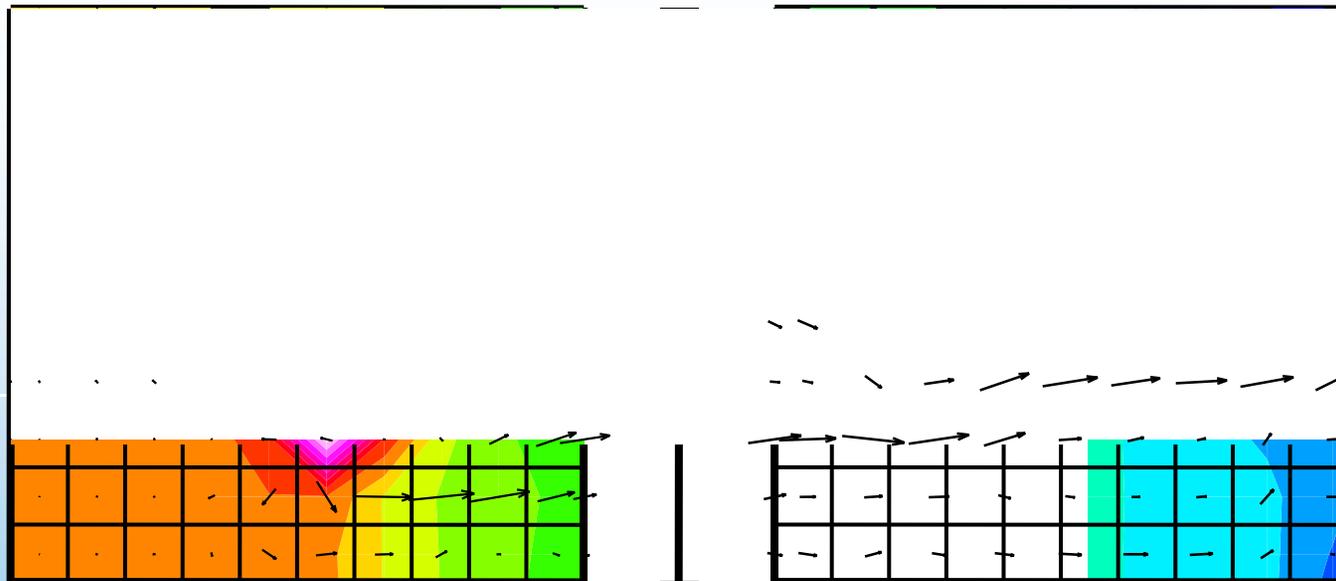


Step 2: Compute the pressure and fluid velocity on each block **efficiently in parallel**.

Based on **velocity mismatch** on interface, update p .
Efficient due to **small size**.

Domain Decomposition Mortar Methods

CO₂ Reservoir Domain

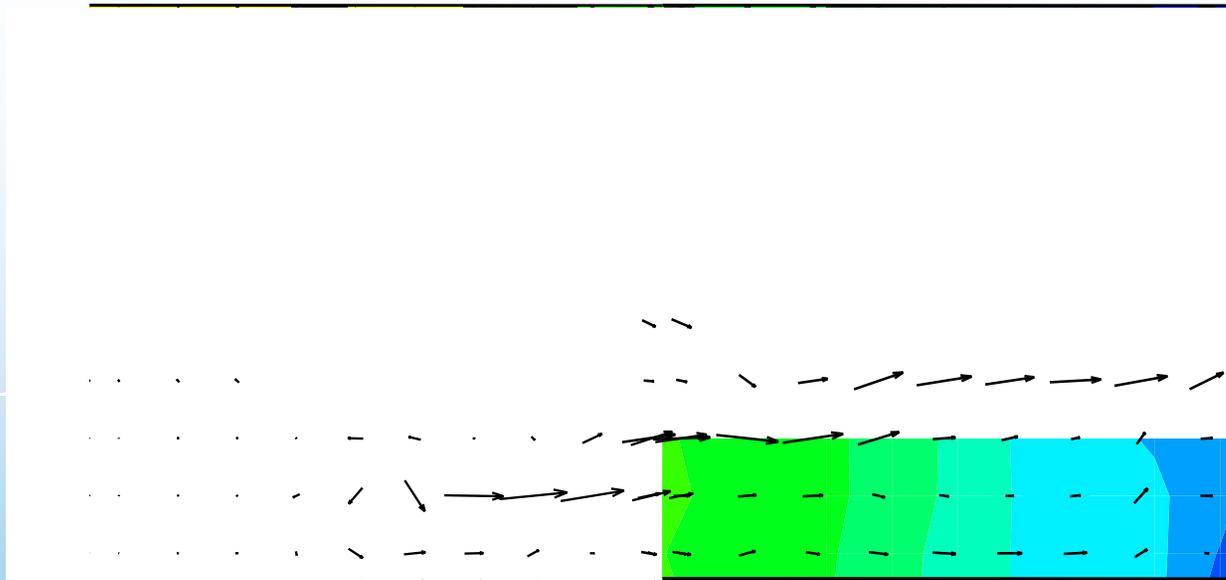


Step 3: Compute the pressure and fluid velocity on each block **efficiently in parallel**.

Done: Negligible **velocity mismatch**.

Domain Decomposition Mortar Methods

CO₂ Reservoir Domain



Pressure and velocity computed efficiently in parallel.

Mortars based on Homogenization Theory

Difficulty. Rock **heterogeneity**, i.e., fine-scale variation in permeability, leads to fine-scale variation in pressure and velocity.

Problem. Polynomials do not approximate rough functions well.

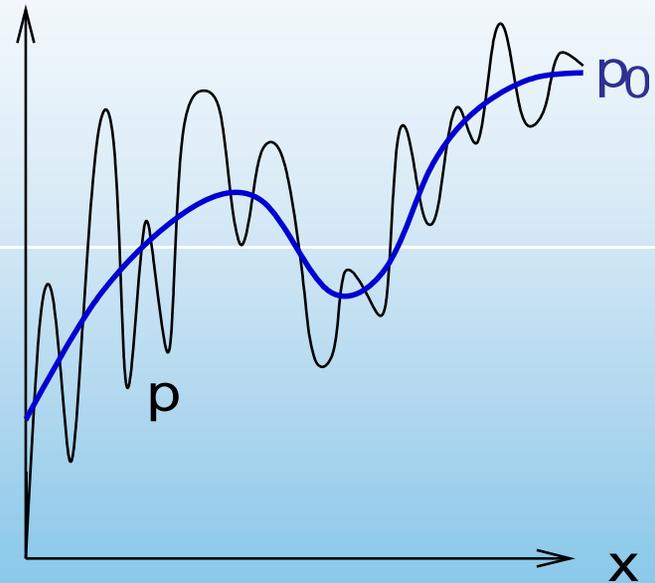
Idea. **Homogenization theory** tells us that

$$p \approx (1 + \omega \cdot \nabla)p_0$$

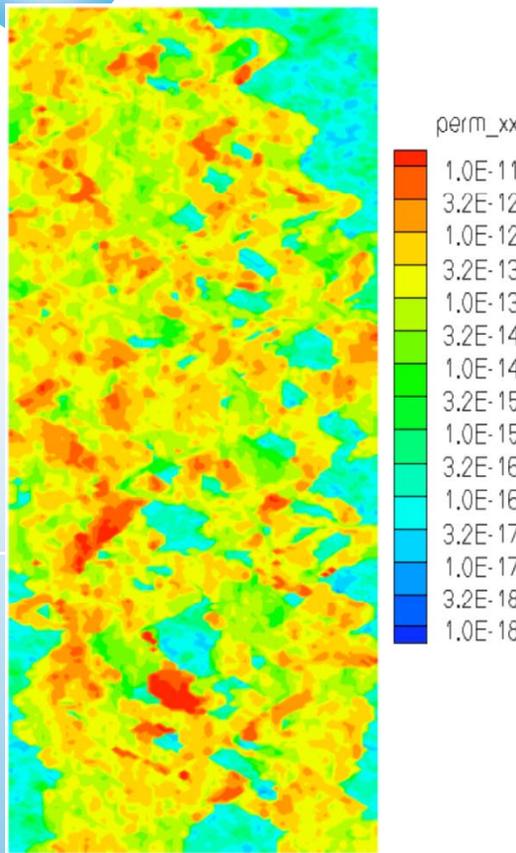
where p_0 is smooth. So approximate

$$\lambda \approx (1 + \omega \cdot \nabla)q$$

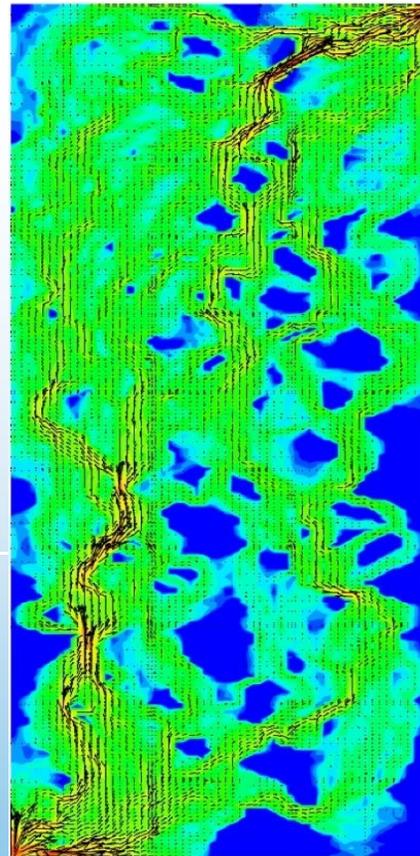
where $q(x)$ is a polynomial.



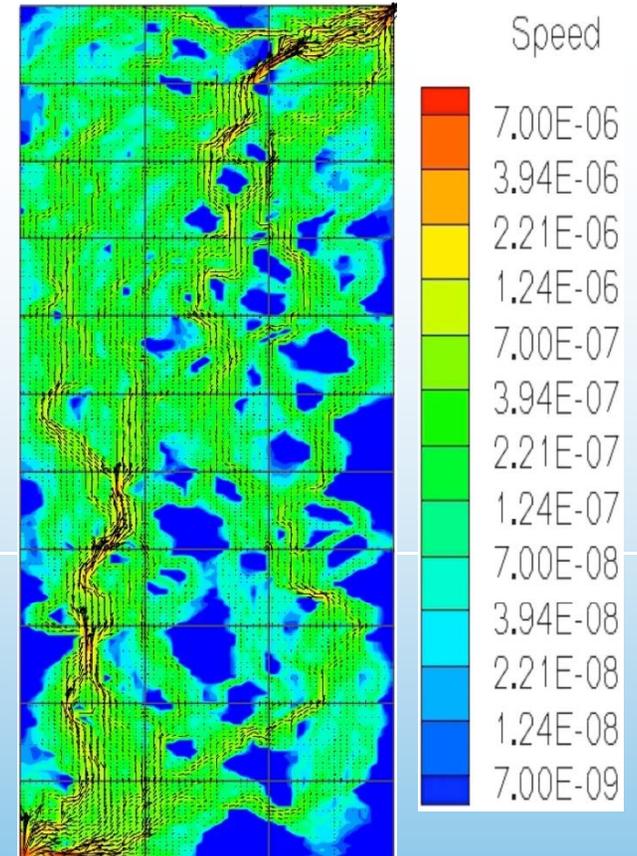
Numerical Test Results



Fluvial
Permeability
(channelized)



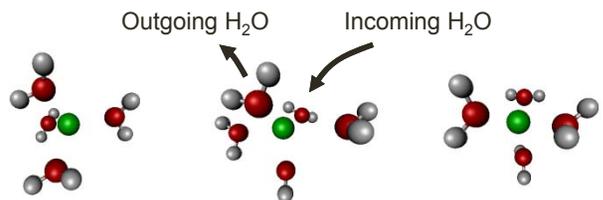
Fine-scale fluid velocity
 60×220 grid
Interface = 1040



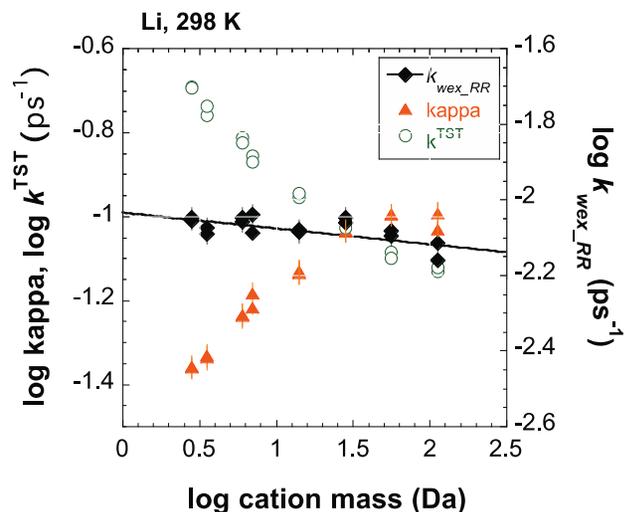
Homogenized mortar
 3×11 subdomains
Interface = 156
Error = 11%



METAL LIGAND-EXCHANGE REACTIONS: A NEW MECHANISM OF KINETIC ISOTOPE FRACTIONATION



Snapshots (taken at ~100 ps intervals) of ${}^7\text{Li}^+$ and the water molecules in its first solvation shell during a water-exchange event. The central image shows a short-lived 5-fold coordination that occurs during the event.



Reaction rate theory predictions of $\log k_{wex}$ vs. $\log m$ for Li^+ isotopes. According to the theory, $k_{wex} = \kappa k_{TST}$, where the transition-state theory constant k_{TST} has an inverse square root dependence on metal-ion reduced mass (green circles) and κ is a transmission coefficient with a poorly characterized mass dependence (orange triangles). Our reaction rate theory calculations show that the mass-dependence of κ almost cancels that of k_{TST} , such that $k_{wex} \propto m^{0.05}$, in agreement with our MD simulation results.

Scientific Achievement

The water-exchange rate k_{wex} of aquated metals decreases with increasing isotopic mass. This type of kinetic isotope effect had never been previously shown.

Significance and Impact

Any reaction that involves a rate-limiting metal desolvation step (or more broadly, a ligand exchange step) may cause significant kinetic isotope fractionation. This includes carbonate precipitation and several other types of reactions (metal adsorption, binding to organic ligands, interfacial redox reactions).

Research Details

- Molecular dynamics simulations of a single metal ion (Li, K, Rb, Ca, Sr, Ba) in liquid water at 5, 25, and 50°C.
- For all solutes studied, $k_{wex} \propto m^{0.05 \pm 0.01}$.
- MD simulation results are consistent with reaction rate theory calculations.
- Results are consistent existing measurements of kinetic isotope fractionation during metal binding to mineral surfaces and organic ligands.

Hofmann A.E., Bourg I.C., DePaolo D.J. Ion desolvation as a mechanism for kinetic isotope fractionation in aqueous systems. *Proceedings of the National Academy of Sciences of the U.S.A.* 109, 18689-18694 (2012).



Predicting Large CO₂ Adsorption in Aluminosilicate Zeolites for Postcombustion Carbon Dioxide Capture

Scientific Achievement

Development of a computational approach to identify the Si:Al ratio in a zeolite structure that maximizes the CO₂ uptake.

Significance and Impact

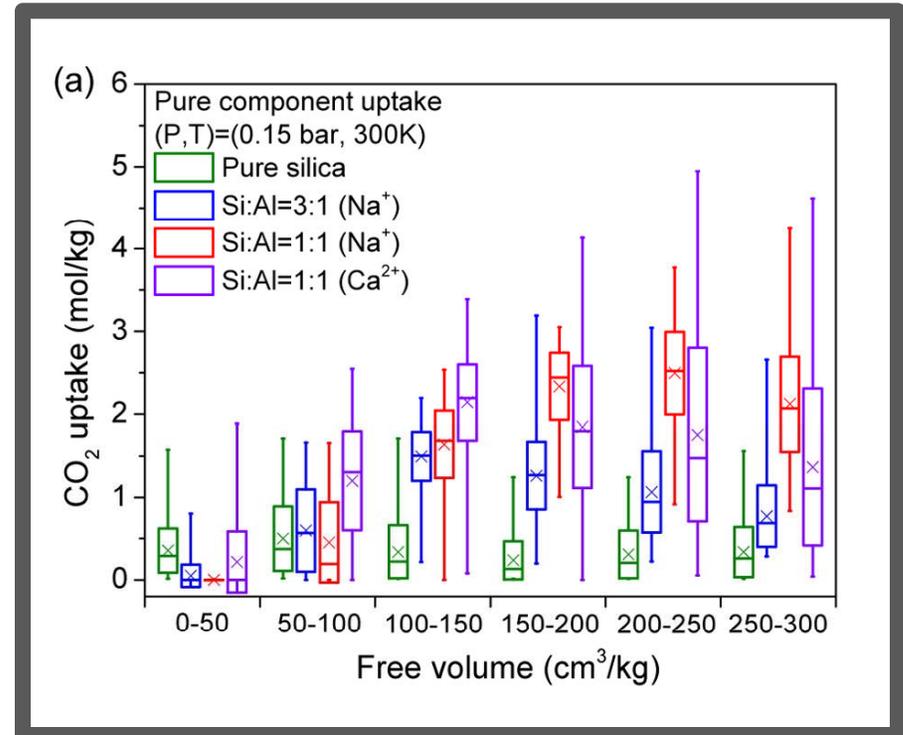
Better understanding of those molecular factors that contribute to a maximum CO₂ uptake.

Research Details

- Development an efficient GPU-based Monte Carlo algorithm that gives a complete isotherm within a few minutes.
- Structures that have an maximum loading have as common features: a large free volume combined with a large number of adsorption sites at a distance 3.0-4.5 Å.

Kim, J.; Lin, L.-C.; Swisher, J. A.; Haranczyk, M.; Smit, B.. *J. Am. Chem. Soc.* 2012, **134** (46), 18940-18943.

Work was performed at the UC Berkeley and LBNL



CO₂ uptake as a function of the free volume and Si:Al ratio: Box plot of CO₂ uptake at 0.15 bar obtained from GCMC simulations for pure-silica (green), Si:Al = 3:1 (Na⁺) (blue), Si:Al = 1:1 (Na⁺) (red), and Si:Al = 1:1 (Ca²⁺) (purple) as a function of free volume for six FV intervals with 400 predicted zeolite structures per interval. Each box represents from lowest to highest the minimum, average minus one standard deviation, median, average plus one standard deviation, and maximum uptake. Cross symbols represent the average CO₂ uptake values.



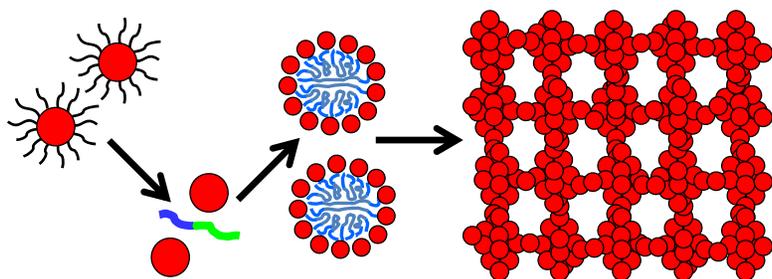
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Center for **Gas Separations**
Relevant to **Clean Energy** Technologies

Nanoporous Semiconductors Synthesized Through Polymer Templating of Ligand-Stripped CdSe Nanocrystals



CdSe nanocrystals + diblock copolymer

Schematic illustration of an evaporation induced self-assembly process that leads to nanoporous CdSe materials. In solution, the polymer self-assembles to form micelles, and upon evaporation of the solvent, the micelles coassemble with the ligand-stripped CdSe nanocrystals into a mesostructured organic/inorganic composite. The polymer template is thermally decomposed under inert conditions to produce CdSe that exhibits three-dimensionally interconnected porosity and high surface area.

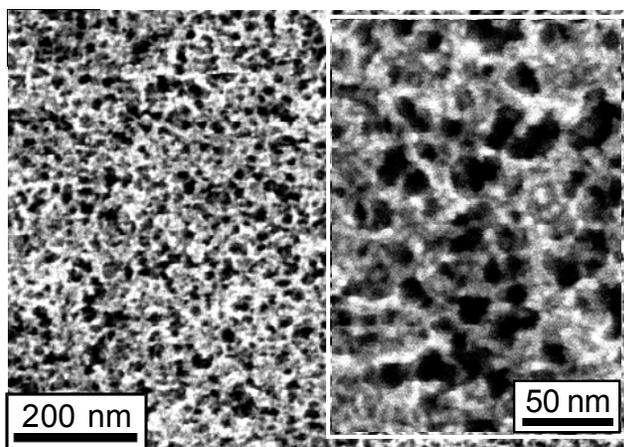
Performers: S. Tolbert and co-workers, University of California, Los Angeles. I. E. Rauda *et al.*, *Adv Mater*, 2013, 10.1002/adma.201203309.

Scientific achievement: Nanoporous CdSe nanocrystal-based materials have been synthesized from ligand-stripped CdSe nanocrystals.

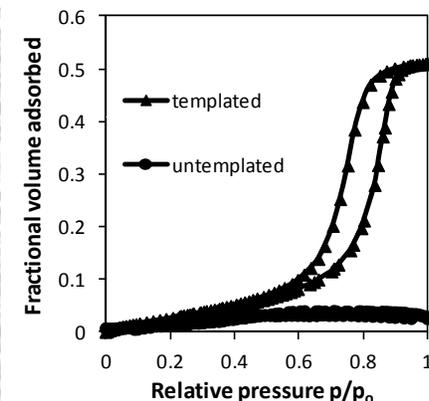
Significance and impact: These nanostructured materials may serve as building blocks for hybrid solar cells. This method should also be directly transferable to other semiconductor or metal nanocrystals amenable to this chemistry.

Research details

- SEM and ellipsometric porosimetry data (above) show nanoporous CdSe exhibits a bimodal porosity with mesopores, created by the polymer template, and micropores arising from the spaces between the nanocrystals embedded in the pore walls.
- These materials have a high surface area with open interconnected porosity, providing good accessibility to the interfacial area.
- Absorption data (not shown) demonstrate mesoporous CdSe preserves quantum confined excitonic features of CdSe nanocrystals.
- Mesoporous CdSe films exhibit reasonable charge carrier mobility, $\sim 10^{-4}$ cm²/V-sec, confirming that the nanocrystals are electronically interconnected.



SEM images of nanocrystal-based mesoporous CdSe.



Adsorption-desorption isotherms for nanocrystal-based CdSe materials.



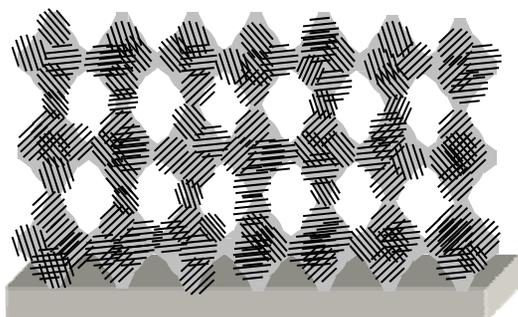
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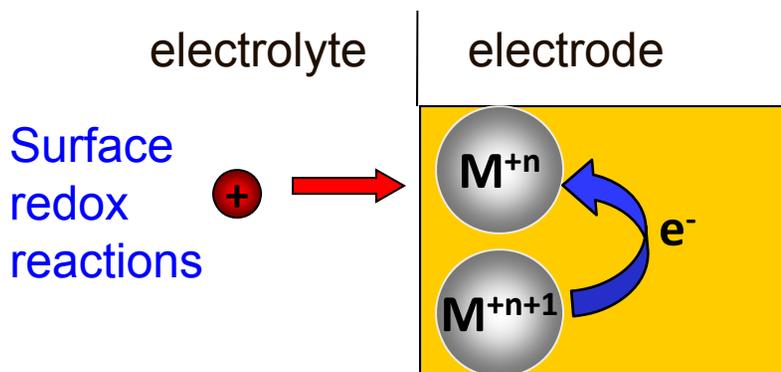
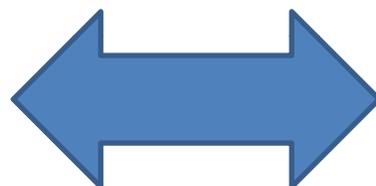
Molecularly Engineered Energy Materials (MEEM)

Porous Supercapacitors



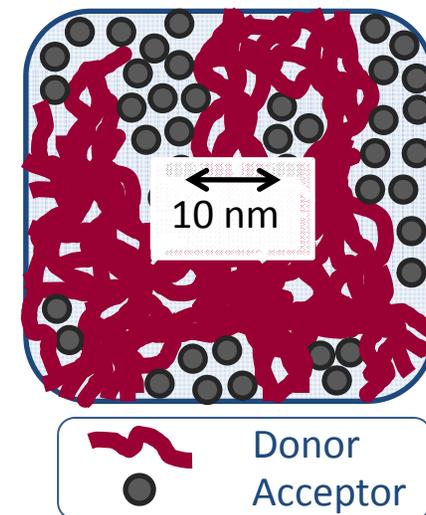
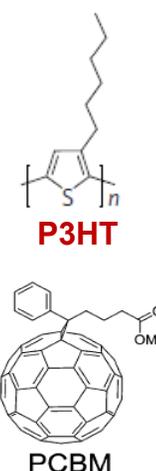
High surface area architectures

Control of
nanoscale
architecture

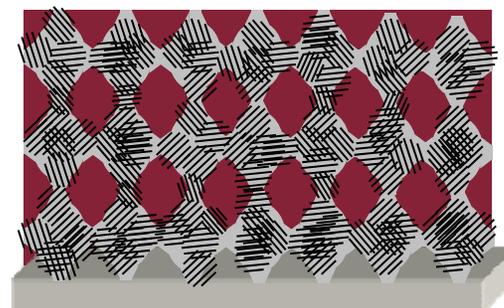


Organic Solar Cells

- Organic bulk heterojunction



- Organic/Inorganic Hybrid



TiO_2 – acceptor
P3HT – donor



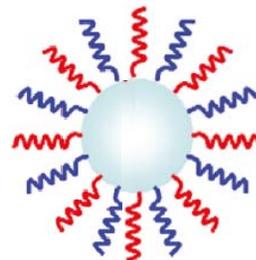
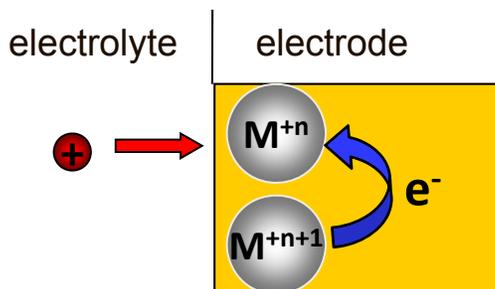
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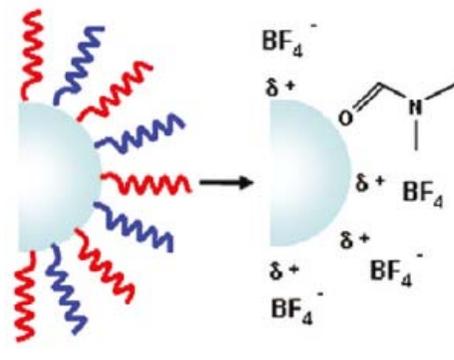
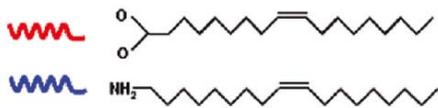
General Method for the Synthesis of Hierarchical Nanocrystal-Based Metal Oxide Mesoporous Materials

Surface redox reactions



- Nanocrystals have high surface area
- Need to remove surface ligands

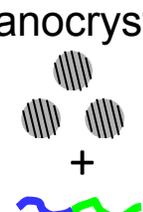
Ligand exchange using NOBF_4 salt to prepare bare nanocrystals



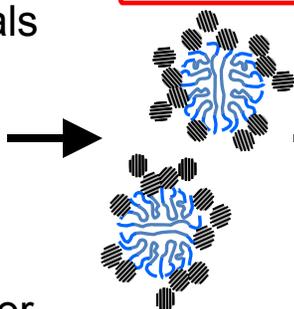
- protonate off ligands
- charge stabilize surface of nanocrystals

evaporation induced self-assembly process

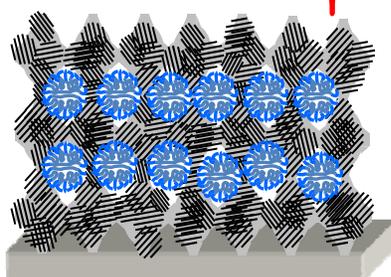
nanocrystals



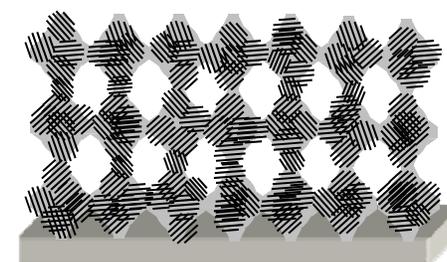
diblock copolymer



self-organization



remove template

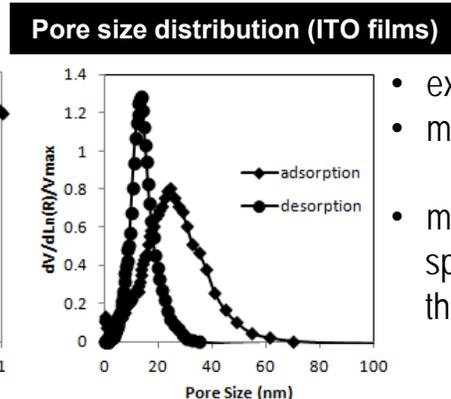
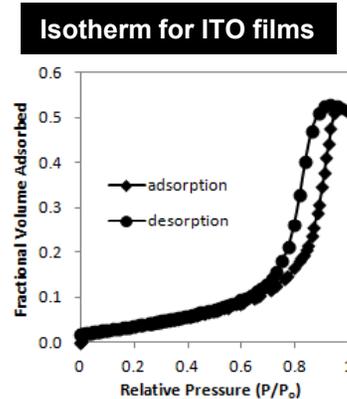
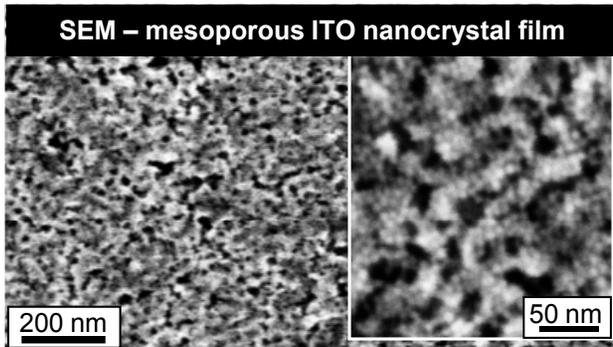


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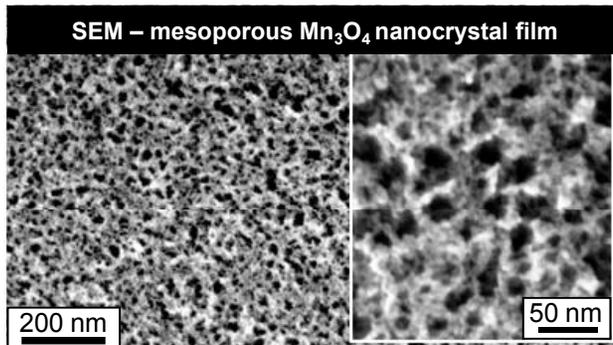
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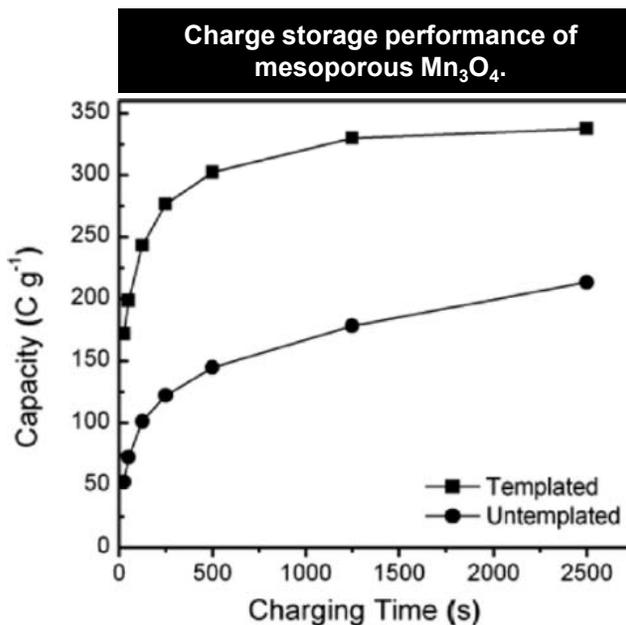
General Method for the Synthesis of Hierarchical Nanocrystal-Based Metal Oxide Mesoporous Materials



- exhibit a bimodal porosity
- mesopores - created by the polymer template,
- micropores - arising from the spaces between the nanocrystals that make up the pore walls



- high surface/interfacial area
- open interconnected porosity



- templated films charge faster and store more charge than untemplated films
- good accessibility for the ions in a liquid electrolyte to reach redox-active sites

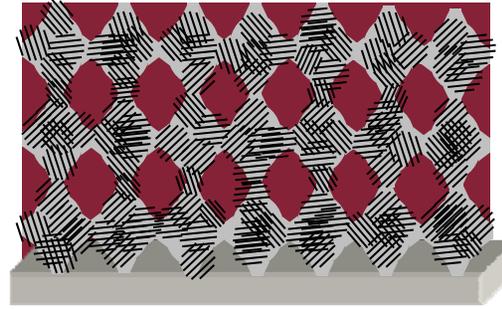


Our Goal is to Extend Our Approach to Photovoltaics

Organic/Inorganic Hybrid solar cell

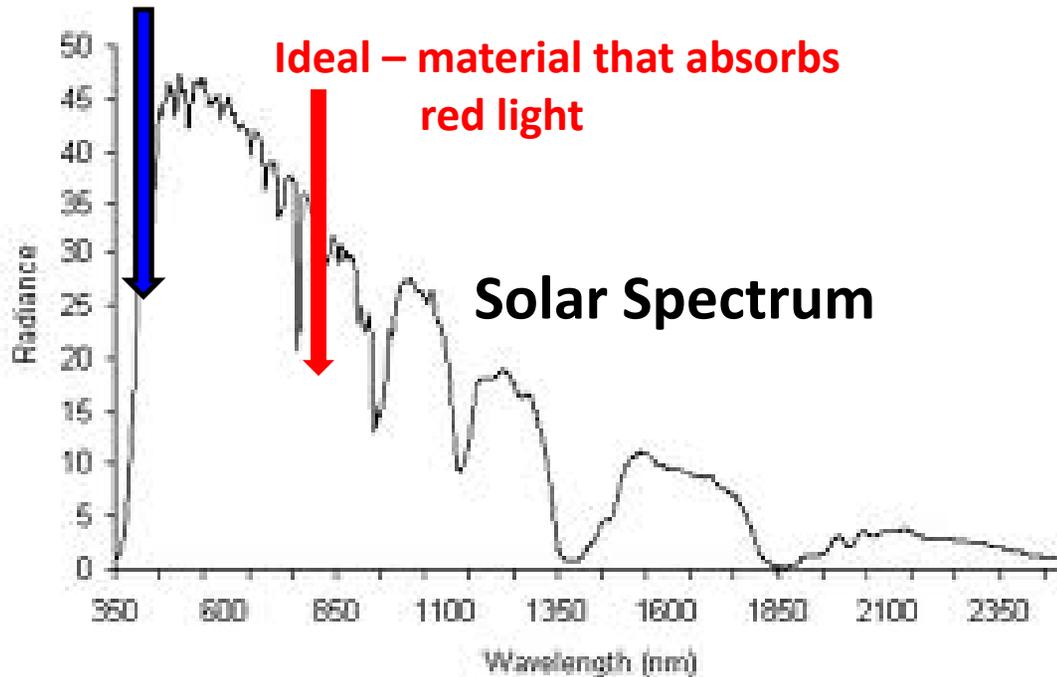
TiO₂ – acceptor

P3HT – donor



- high interfacial area
- accessible volume
- electronically interconnected
- ideal architecture

TiO₂ – absorbs UV light



- syntheses for non-oxide semiconductor nanocrystals are well established
- how can we extend this chemistry to non-oxide systems?



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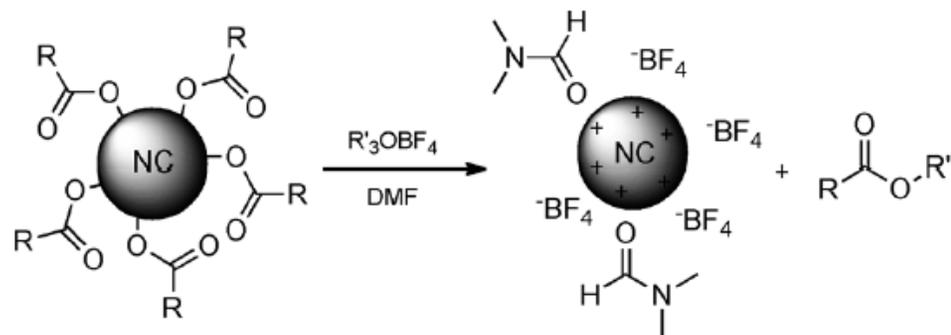
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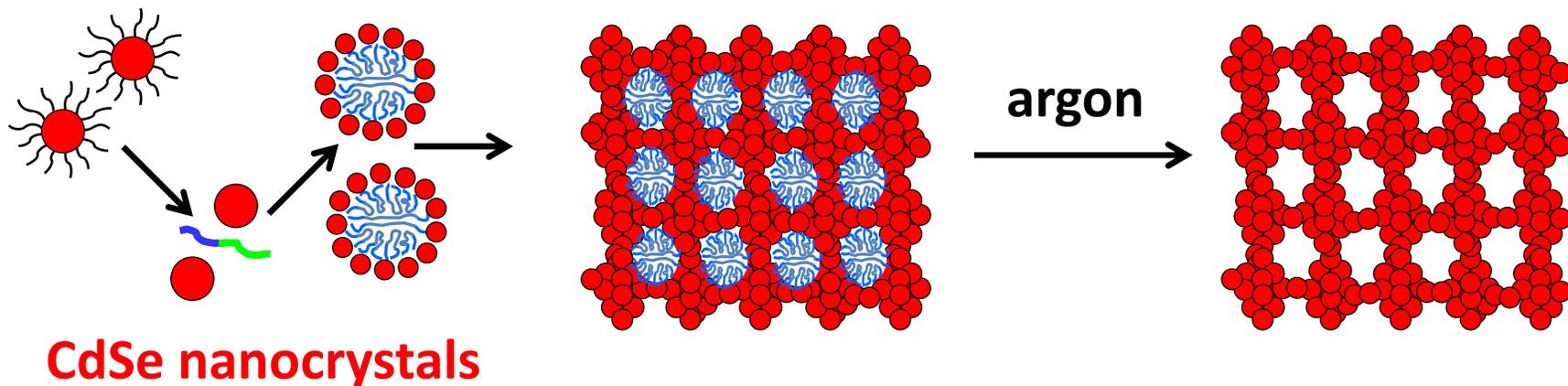
We Can Extend This General Route to Non-Oxide Semiconductor Nanocrystals

- We are going to use CdSe as a model system
- CdSe – absorbs red light

new chemistry yields
bare CdSe nanocrystals
soluble in polar solvents



Rosen, et. al., Angew. Chem. Int. Ed. 2012, 51, 684-689.

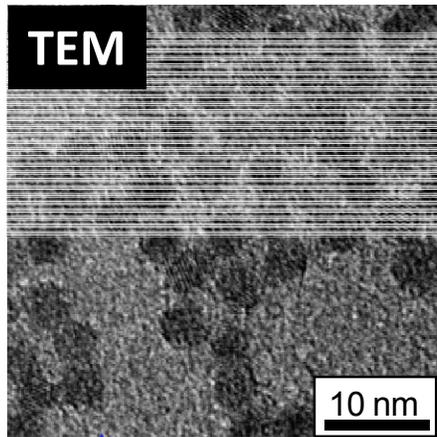


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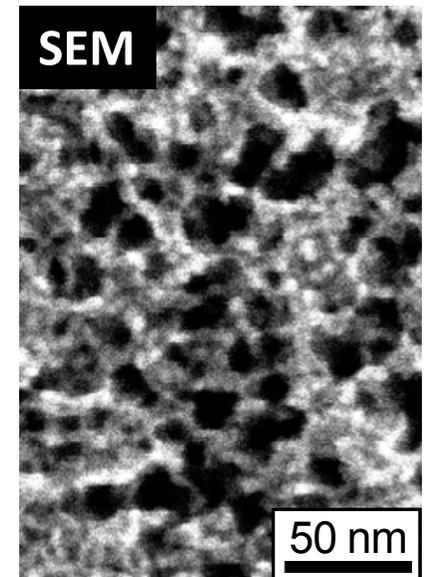
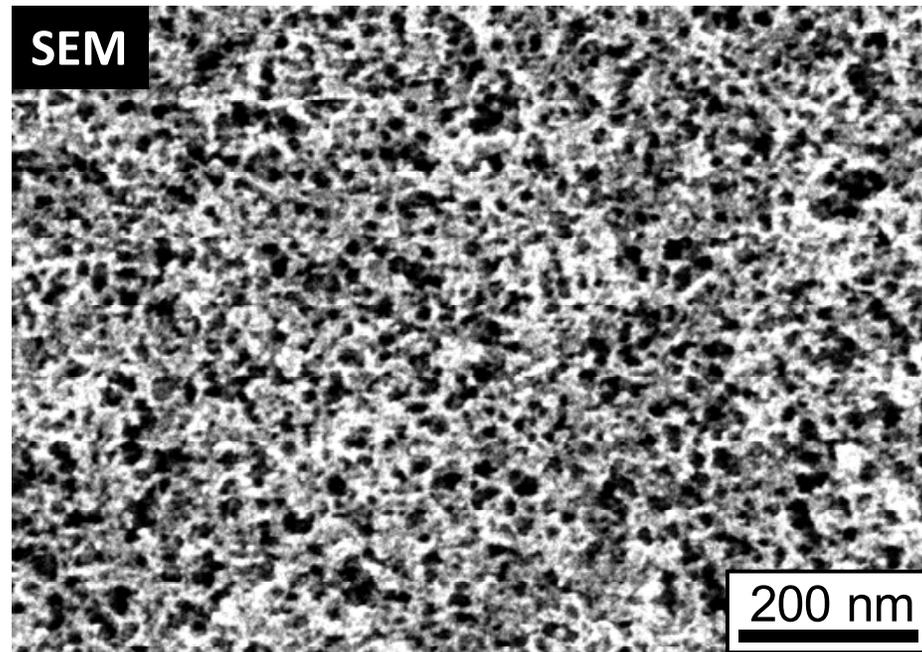
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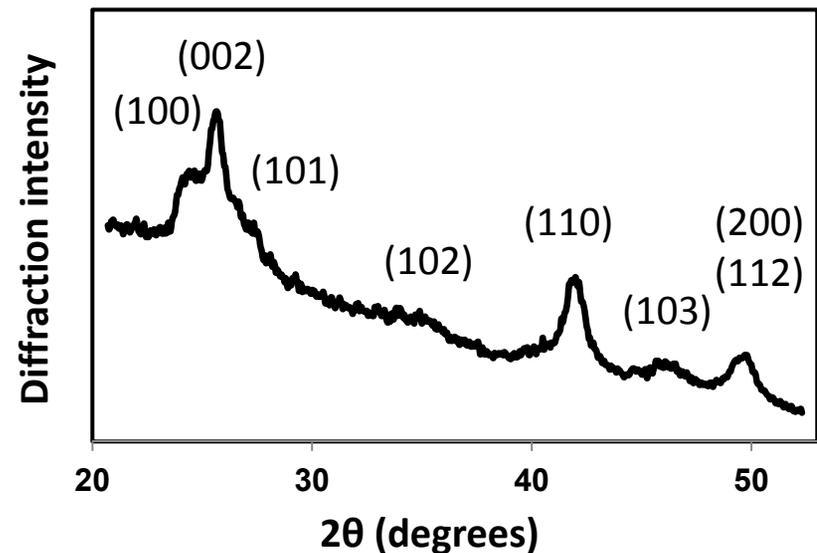
Method Yields Mesoporous CdSe Nanocrystal Thin-film



↑
bare CdSe
nanocrystals



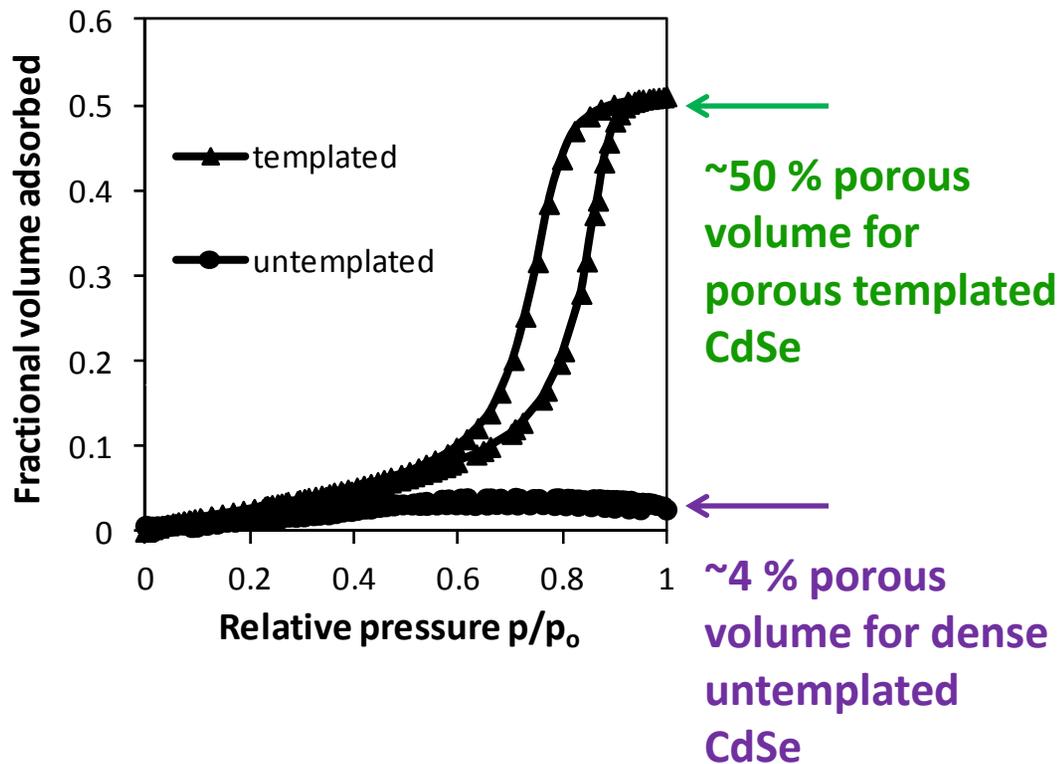
XRD shows mesoporous CdSe
thin-film retains wurtzite
structure after calcination



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Ellipsometric Porosimetry Measurements Show Templated CdSe Films Are Highly Porous

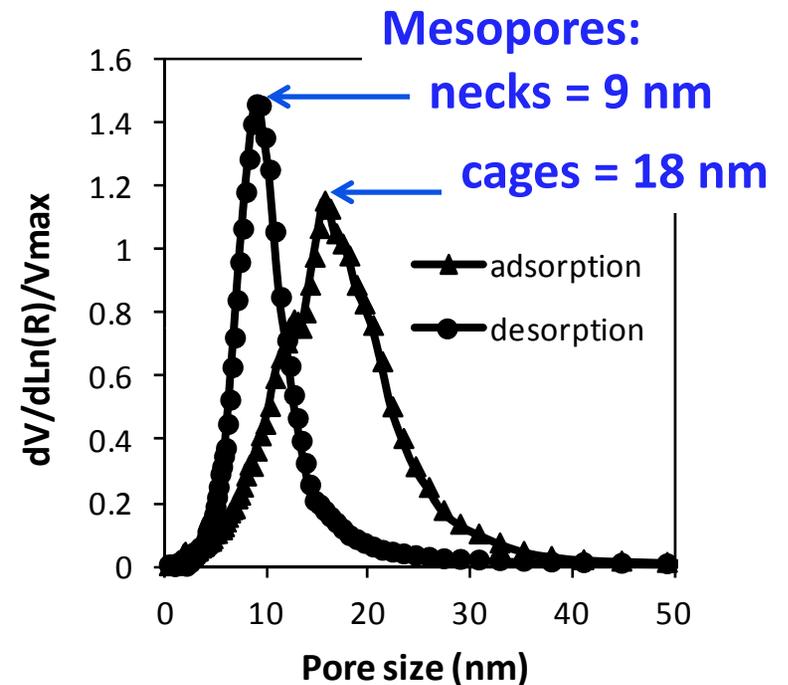


dense untemplated CdSe:

Micropores:

- cages = 2.0 nm
- necks = 1.2 nm

porous templated CdSe



porous templated CdSe:

Micropores:

- cages = 2.0 nm
- necks = 1.8 nm



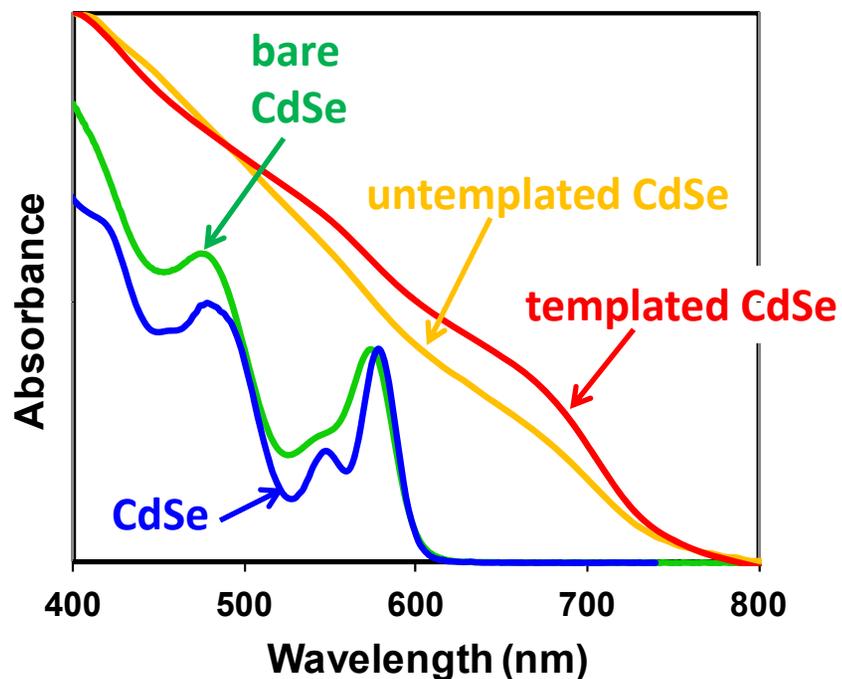
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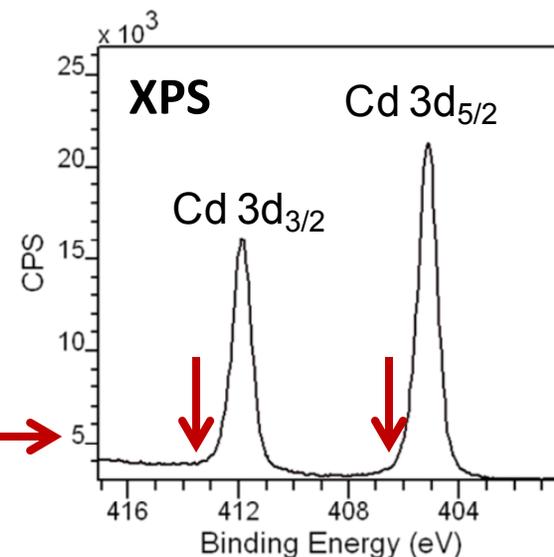
Absorption and Composition of CdSe Nanocrystals are Preserved in Film Form

UV-Vis absorption spectra

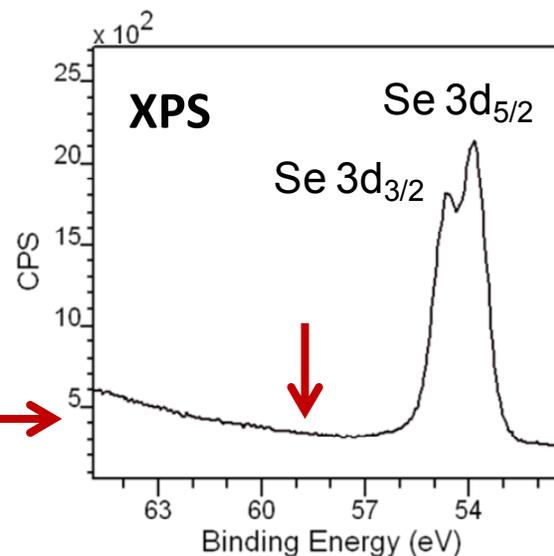


Templated CdSe film preserves excitonic absorption typical of quantum confined nanocrystals

absence of oxidized Cd CdO_x peaks



absence of oxidized Se SeO_2 peak

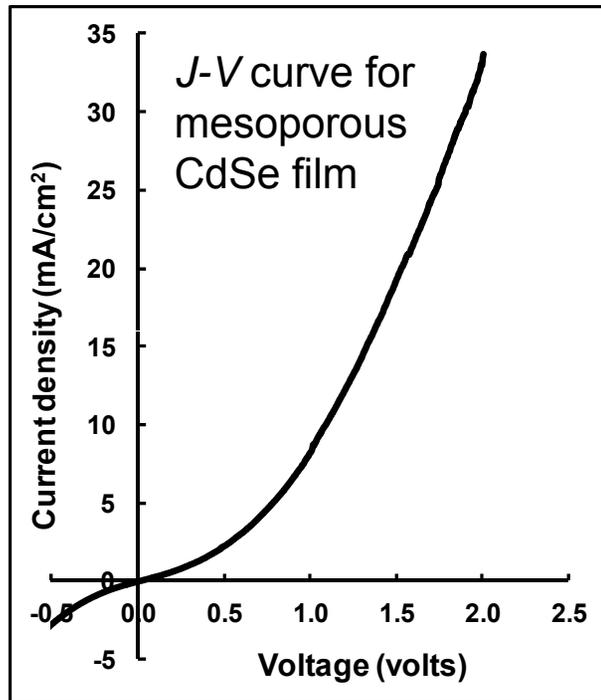


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Templated CdSe Nanocrystal-Based Films are Electrically Interconnected

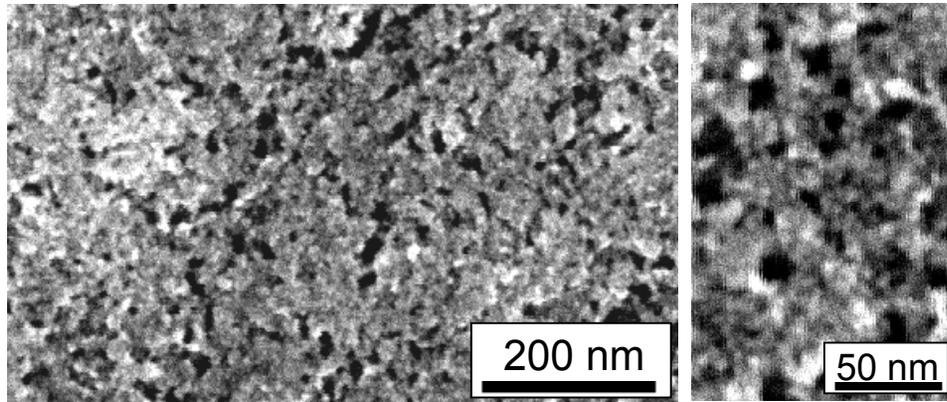


- mobility = 10^{-4} cm²/V-sec
 - the CdSe nanocrystals are electronically interconnected
- **within reported values for CdSe nanocrystal-based solids



We can Template Mixtures of Nanocrystals

Mixed CdSe/Mn₃O₄ System



- the templating process is completely decoupled from the chemistry used to synthesize these nanocrystals
- nanocrystals are mere physical objects or building blocks
- explore other non-oxide and mixed semiconductor systems



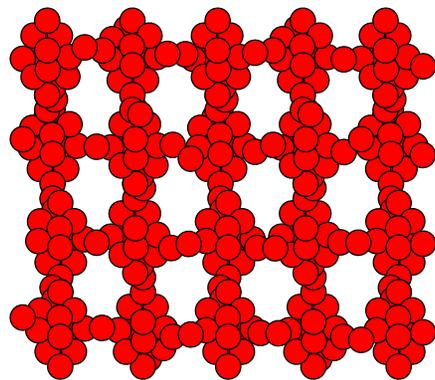
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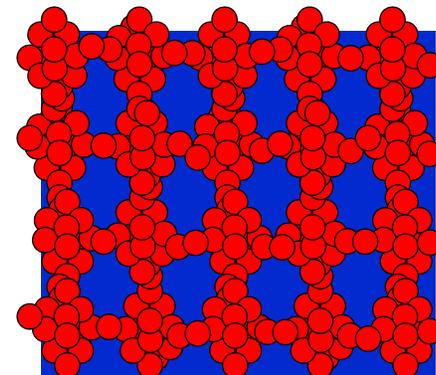
Conclusion and Future Outlook

- Our work on mesoporous semiconductors demonstrates the combination of **high accessible interfacial area** and **interconnected electronic conductivity without oxidation of the semiconductor**
- Our work builds a bridge between the complex architectures of oxides and the electronic and optical tunability of semiconductors
- Future work in our EFRC will focus on hybrid photovoltaic device fabrication:



high surface
area CdSe film

infiltrate pores with
semiconducting
polymer



integrated hybrid
photovoltaic device



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