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Title: Understanding & Optimizing Water Flux & Salt Rejection in Nanoporous Membranes

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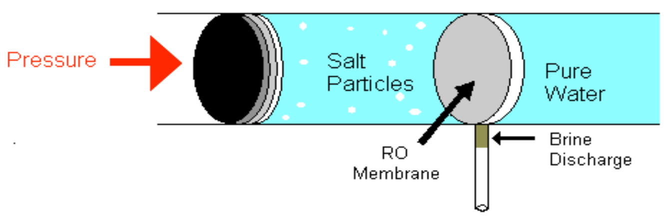
Water Desalination: A Global Problem

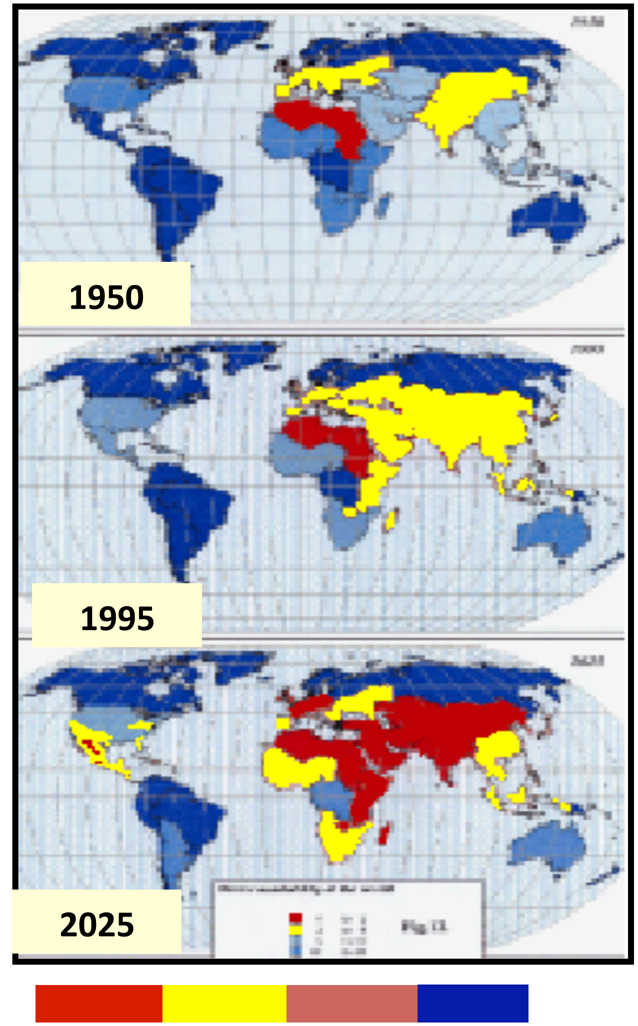
Half the world's population will soon lack clean water:

- causes international tension, public health crises
- water problems linked to energy problems
- desalination by Reverse Osmosis membranes is <u>expensive</u> and produces <u>unhealthy sterile water</u>



A ***breakthrough*** in materials research needed to redesign nanopores for:

- fast (barrierless) water transport
- select ion exclusion (mineral water)



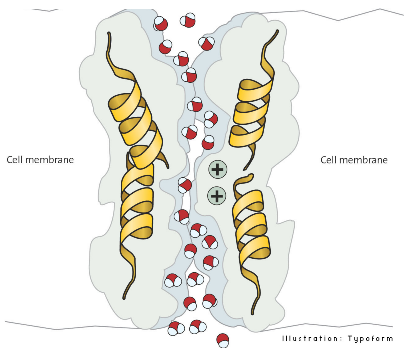
shortage

> **"Water promises to be to the 21st century what oil was to the 20th century: the precious commodity that determines the wealth of nations."**
> *Fortune Magazine, May 15, 2000*

Innovative Approach to Designer Membranes:

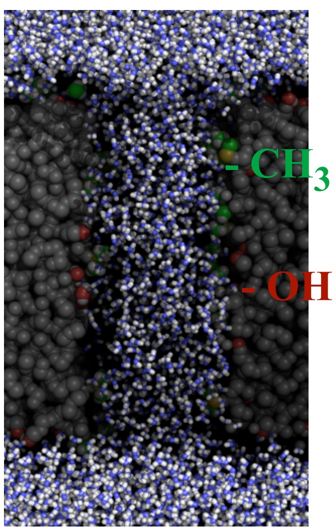
Discover rules for water filtration in Nature's membranes

Biological channels



• transport H_2O fast & select minerals

Model channels



• Bio-inspired design

• Theoretical modeling of mechanisms

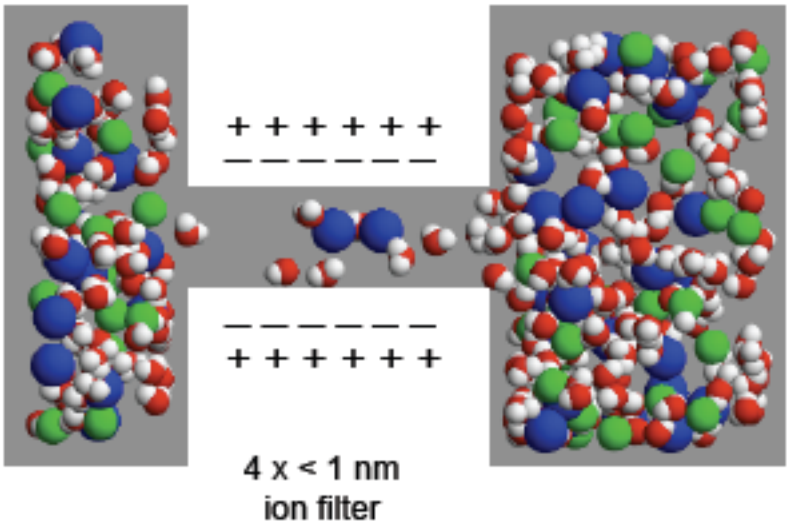
• Inorganic membrane synthesis

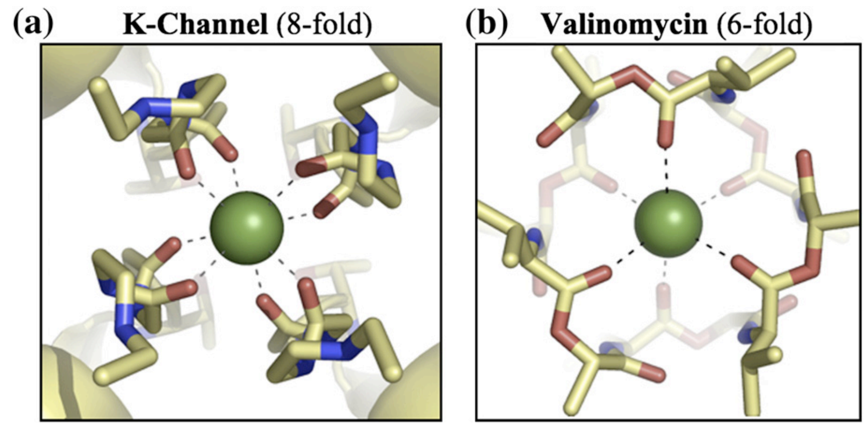
< 30 A
pore diameter

Solution: Harness molecular biomechanisms.
Expect 10x increase in water flux.
Expect select minerals for health.

Approach: Couple molecular theory + experiment.
Theory to predict rules (structure vs function).
Experiment to construct nanoporous structures.
Experiment to validate predictions.

3 Molecular Mechanisms for Select Ion Filtration





• Dense dipoles on biological channel walls:

a) no dipoles or alternating dipoles rejects salts
b) ion-wall interactions *not* screened by water in narrow pores

• Biological binding sites that select K^+ over smaller Na^+ ions:

a) Channel uses <u>special environment</u> & <u>specific number</u> of coordinators
b) Molecule uses <u>rigid cavity size</u>

Bimodal Acid-base Behavior on Silica Affects Desal

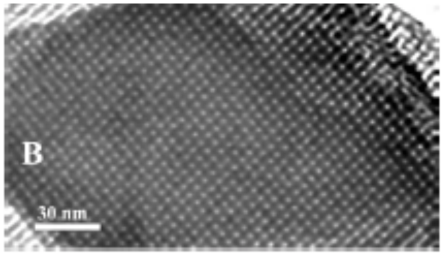
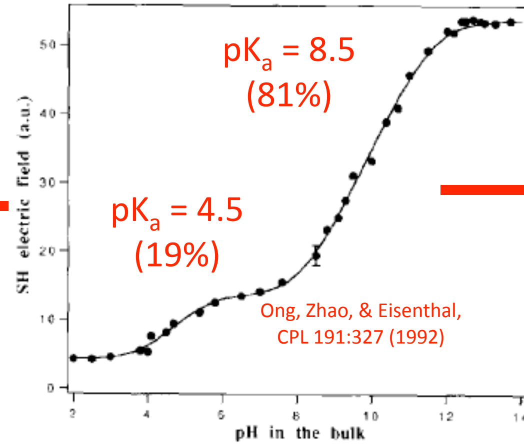
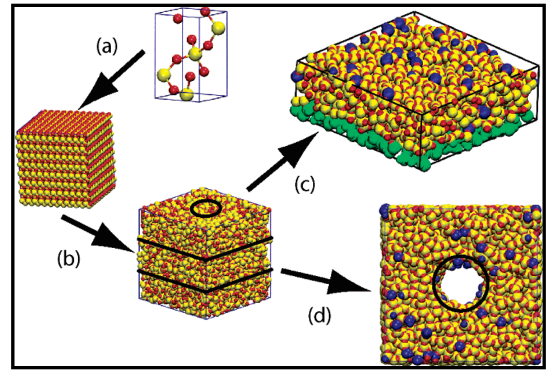


Fig. 2 TEM images of sample c with cubic mesostructure: (A) [111] direction; (B) [100] direction. Inset is electron diffraction pattern for A.

- nanopore surface charge governed by SiO^- density
- affects Na^+/Cl^- rejection



- SiO^- density depends on 2 acid-base pK$_a$



- thus knowledge of low pK$_a$ SiOH structure critical for modeling Na^+/Cl^- rejection

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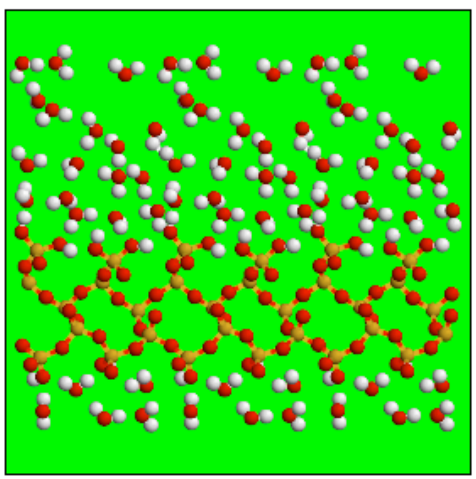
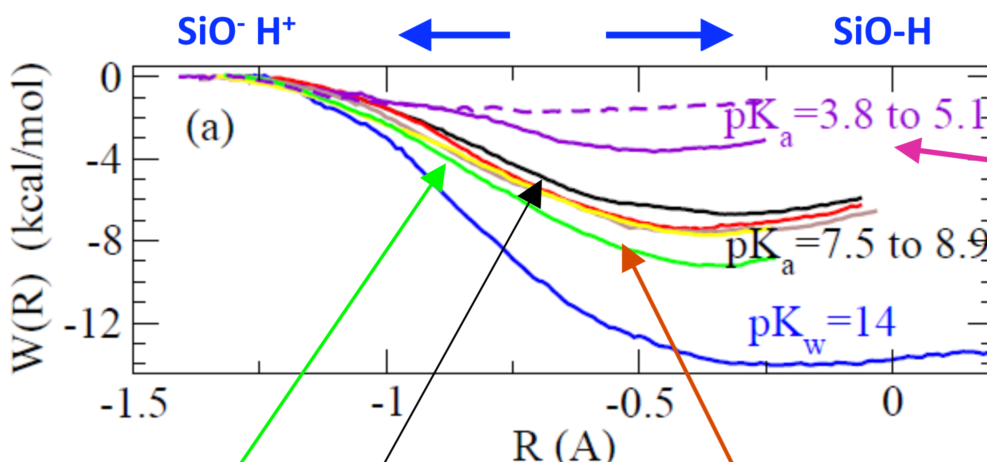
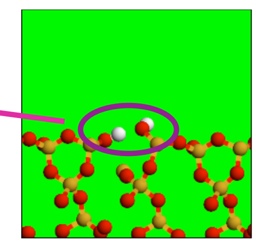
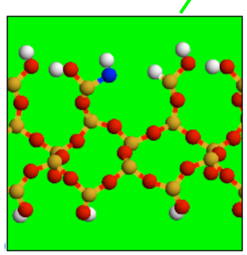
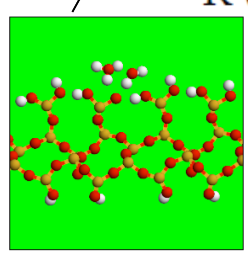
AIMD simulations:
liquid water/SiO_2

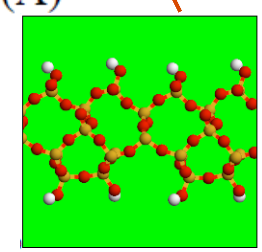






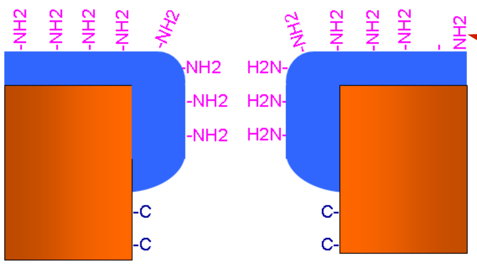




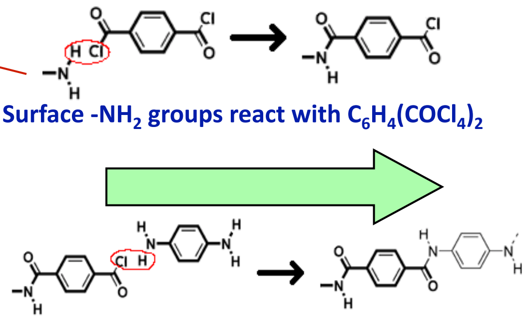


- structural motifs in literature incorrect;
- low pK$_a$ only on strained surfaces

Construct Biomimetic Inorganic Peptide Channels by Liquid-State ALD Nanofabrication

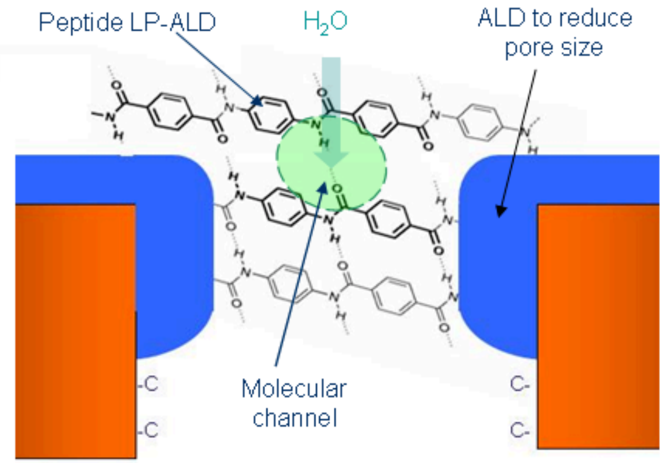


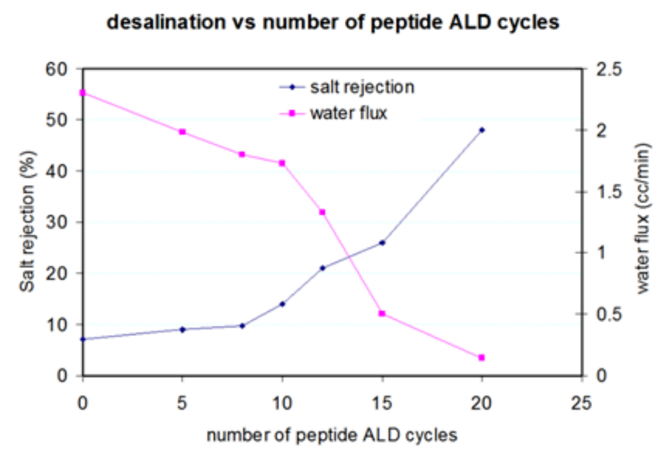
Starting with B56 mesoporous silica supported on AO disc and modified with amine groups $–NH_2$



Surface $-NH_2$ groups react with $C_6H_4(COCl_4)_2$

then react with $C_6H_4(NH_2)_2$ and repeat these steps





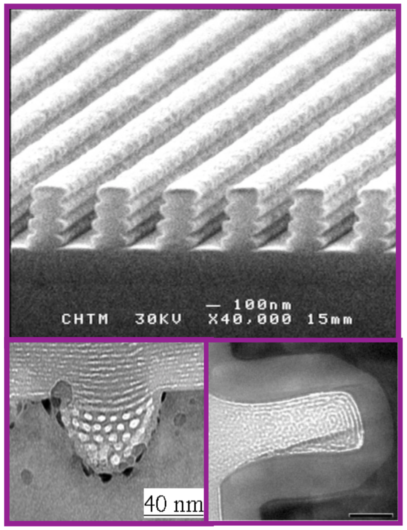
- *single pore surface chemistry such as* $–NH_2$ only shows moderate salt rejection
- Inspiration from natural channels: constructed with proteins that contains not only amino groups, but also carboxyl groups → **interplay between amino and carboxyl groups is important for desalination process**

→ Fabricate peptide nano-channels containing both amine and carbonate, excellent desalination performance has been achieved

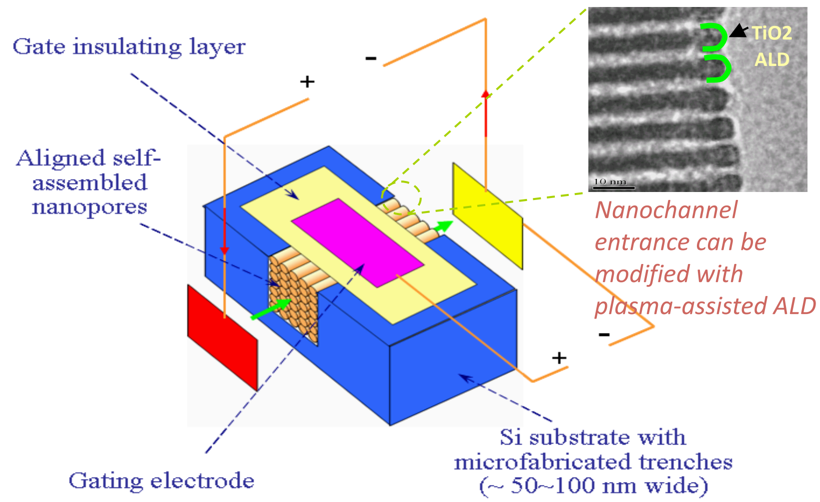
a) schematic of ALDed Peptide on nanopores; b) the water desalination measurements of nanopores decorated with peptide.

Develop New Platforms to Measure Ion Transport

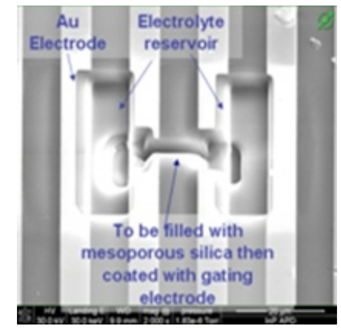
Nanofluidic FET-type device



a) SEM image of parallel nano-trenches; b) and c) Mesoporous silica in nanotrenches are aligned along the trenches, ideal channels for modeling and theoretical study



SEM image of a device being fabricated by FIB

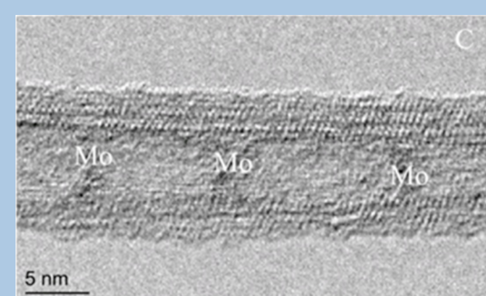


Advantages:

- May apply a gating bias to control the transport of ions through the nanopores,
- Can determine the potential needed to gate the transport of an ion
- Maybe combined with Hall effect

Hydrophilic titanate nanotube: single nanotube based device

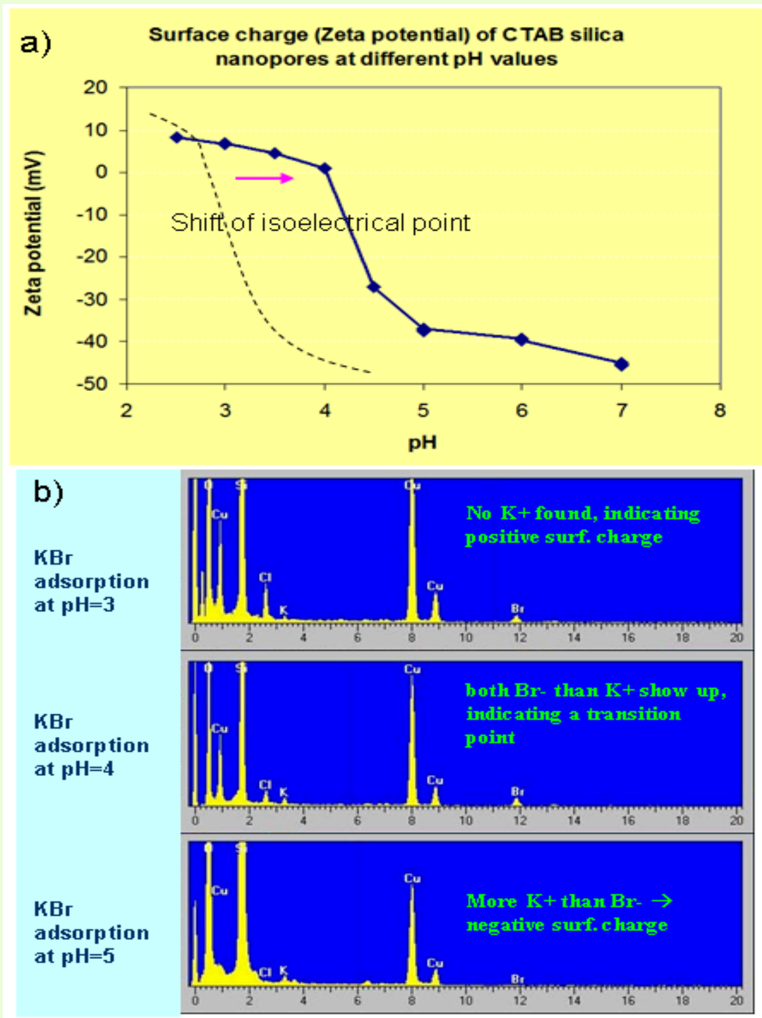
- Ideal atomic level surface smoothness like CNT
- Hydrophilic-surface chemistry can be easily modified, and water enters spontaneously, unlike CNT.
- easy to manipulate to fabricate a single tube-based device.
- mimics hydrophilic channels such as aquaporin filters
- Device can be fabricated by FIB using a similar platform as shown above



High-resolution TEM image showing the crystal lattice of ta titanate nanotube and Mo –docoration – indicating a smooth surface and tunable surface chemistry

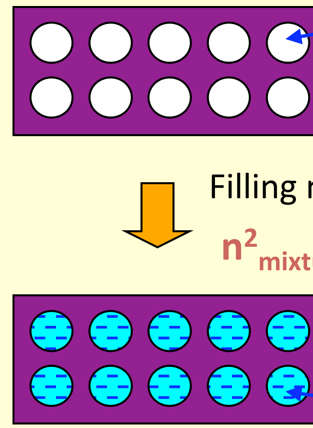
“Unusual” Aqueous System Found within Nanopores

Shift of silica isoelectric point in nanopores



a) Zeta potential measurement of mesoproous silica at different pH; b) EDS data of KBr adsorption in mesoporous silica at different pH

Reduced refractive index of water in nanopore

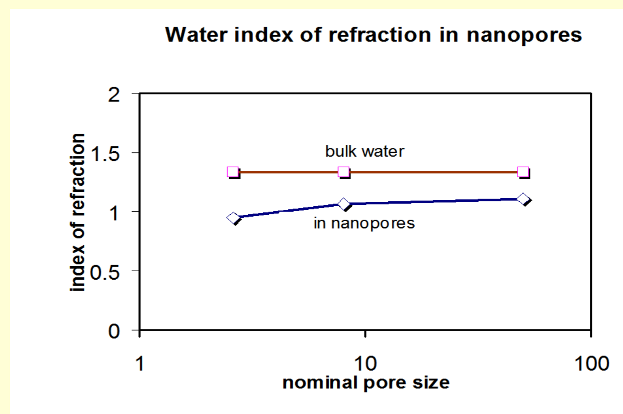


Air, n=1

Filling nanopores with water

$$n^2_{mixture} = x_1*n_1^2 + x_2*n_2^2$$

Bulk water
n=1.33



Water confined in nanopores has reduced refractive index/dielectric constant

Summary & Publications

- **Accomplishments**
  - Identify molecular mechanisms in Nature + translation strategies
  - Nanofabricate ion selectivity filters
  - Discover determinants of fast ion/water conduction in nanopores
  - Develop new platforms to measure ion conduction in nanopores

- **Publications**
  - **Varma & Rempe *BJ* (2007)**
  - **Jiang, Brinker *et al. JACS* (2007)**
  - **Varma, Sabo & Rempe *JMB* (2008)**
  - **Varma & Rempe *JACS* (2008)**
  - **Leung *JACS* (2008)**
  - **Leung & Rempe *JCTN* (2009)**
  - **Singh, Brinker, *et al JCP* (2009)**
  - **Lorenz, Rempe *et al JCTN* (2009)**
  - **Brinker *et al Nature Mat* (2009)**
  - **Leung, *et al Science* (submitted)**

Biology ⟷ Inorganic Nanostructures
Molecular Modeling ⟷ Molecular Synthesis