Understanding & Optimizing Water Flux & Salt Rejection in Nanoporous Membranes

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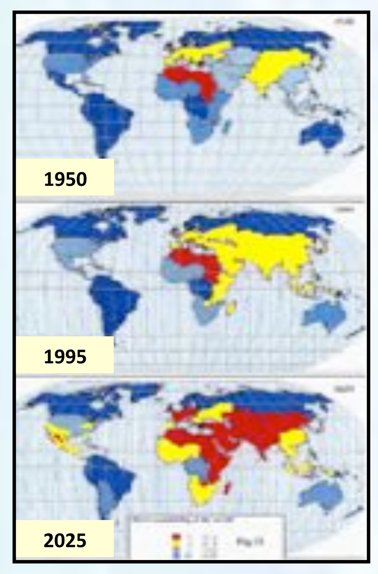
Problem

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 expensive and produces unhealthy sterile water

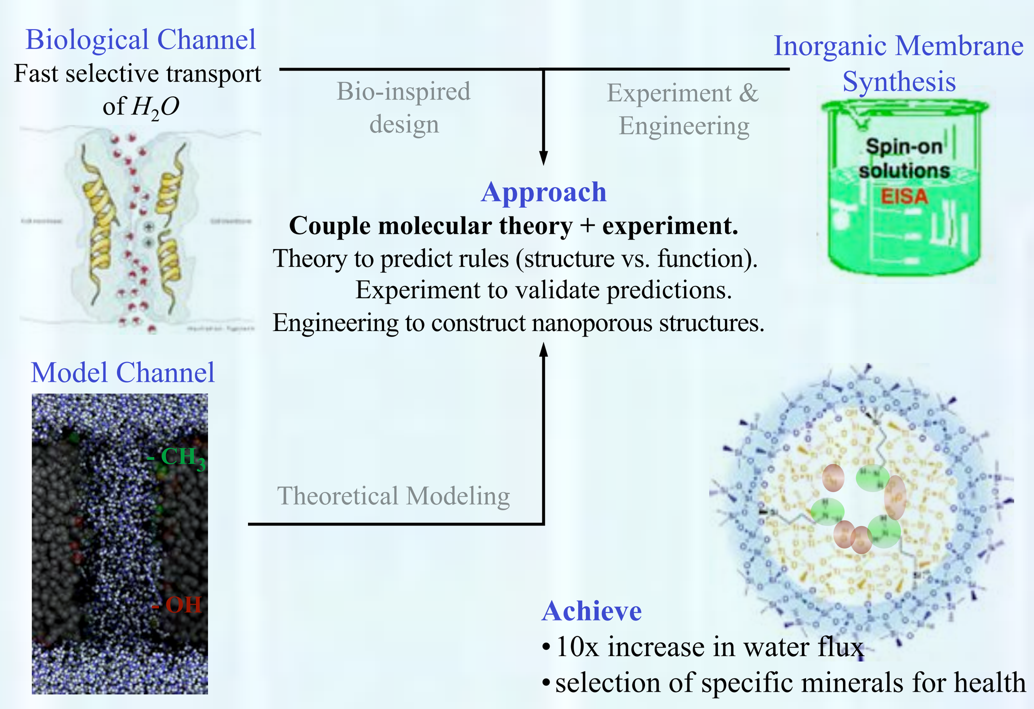


A breakthrough in materials research needed to redesign nanopores for:

- fast (barrier-less) water transport
- select ion exclusion (mineral water)

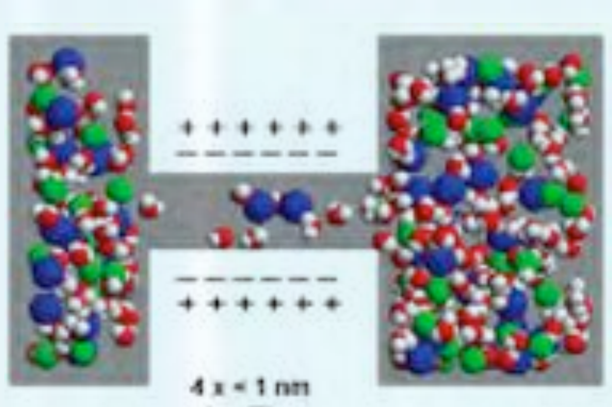
"Water promises to be to the 21st century what oil was to the 20th century: the precious commodity that determines the wealth of nations." *Fortune Magazine, May 15, 2000*

Innovative Approach to Designer Membranes: Discover Rules for Water Filtration in Nature's Membranes



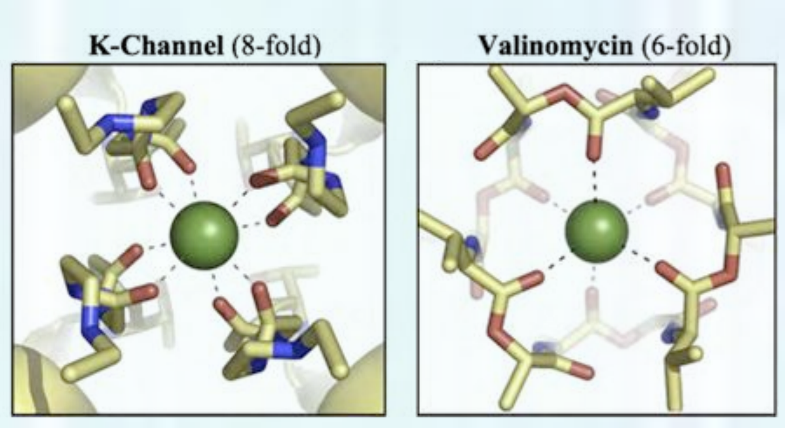
Approach

Molecular Mechanisms for Select Ion Filtration



Dense dipoles on biological channel walls:

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

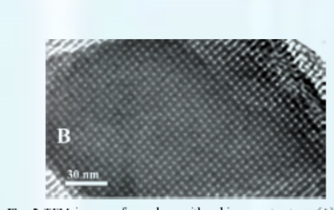


Biological binding sites that select K^+ over smaller Na^+ ions:

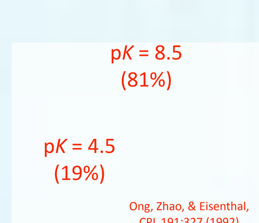
- Channel uses special environment & specific number of coordinators
- Molecule uses rigid cavity size

Results

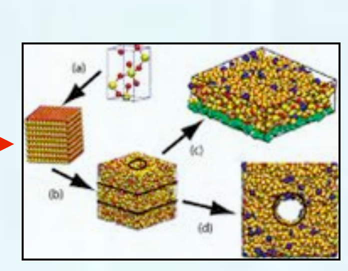
Bimodal Acid-base Behavior on Silica Affects Desal



- Nanopore surface charge governed by SiO^- density
- Affects Na^+/Cl^- rejection



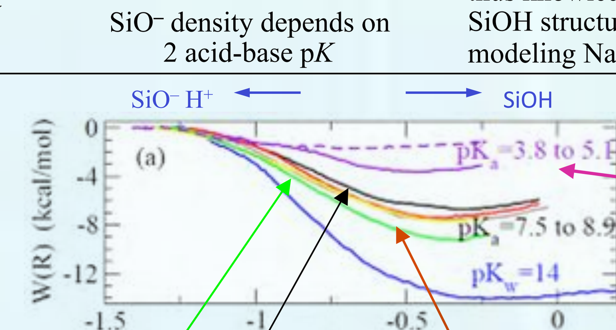
SiO^- density depends on 2 acid-base pK



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

AIMD simulations

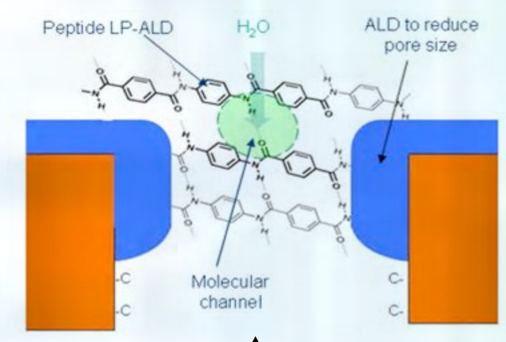
liquid water/SiO_2

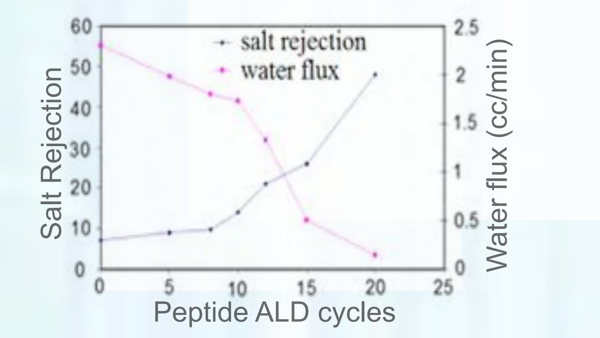


- Structural motifs in literature incorrect
- Low pK only on strained surfaces

Results (cont.)

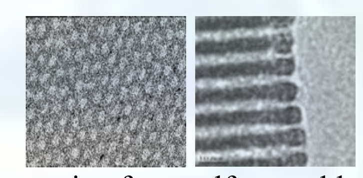
Construct Biomimetic Inorganic Peptide Channels by Liquid-State ALD Nanofabrication





pore modified with $-NH_2$

then carry out peptide ALD

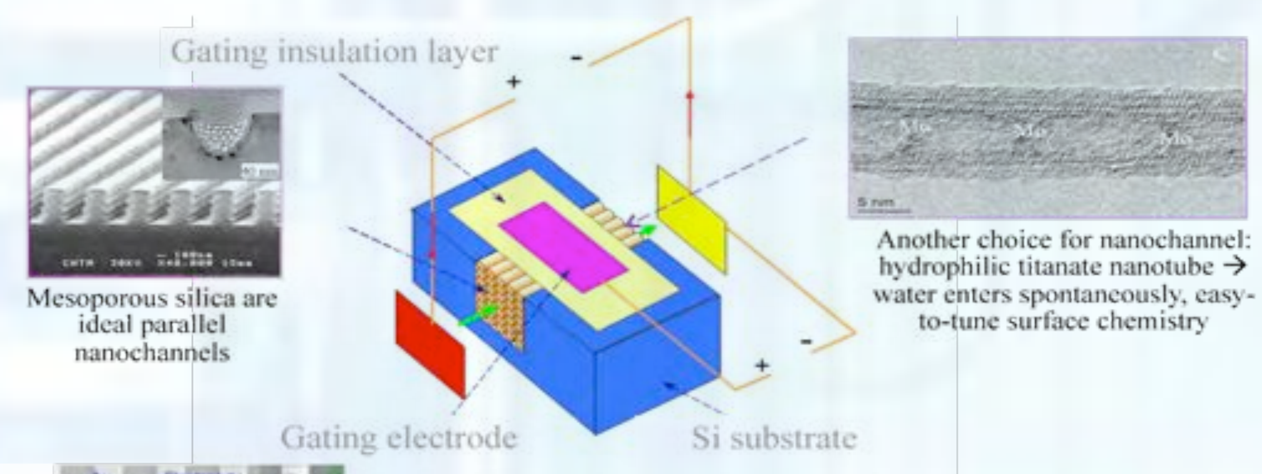


starting from self-assembled mesoporous silica

Inspired by natural channels and guided by theoretical work, peptide water channels were fabricated by liquid-state ALD:

- Excellent salt rejection was achieved
- Interplay between amino groups and carboxyl groups was found to be important for desalination

Develop New Platforms to Measure Ion Transport



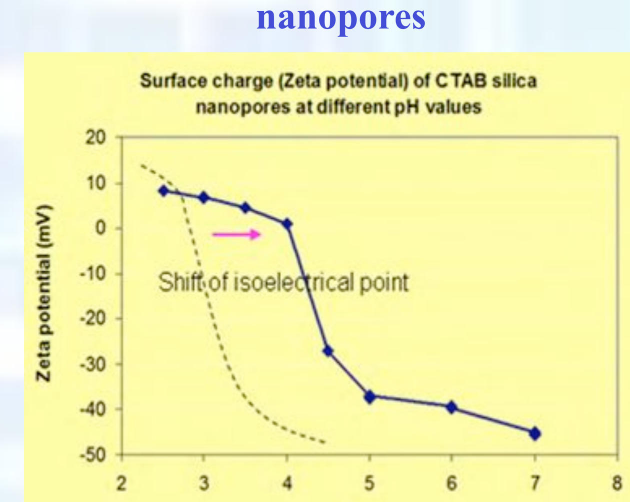
SEM image of a device being fabricated by FIB

Nanofluidic FET-type device

- Gating bias to control & study ion transport within chemically tuned nanopores,
- Single nanotube–based device using hydrophilic titanate nanotube

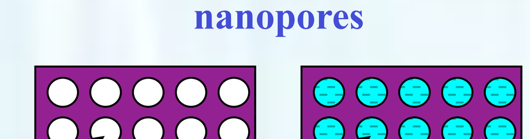
"Unusual" Aqueous System Found within Nanopores

Shift of iso-electric point in nanopores

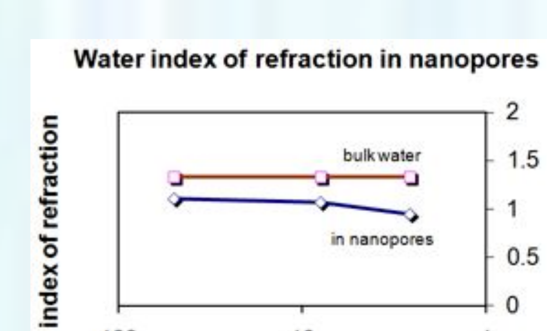


Zeta potential measurement of silica at different pH. Flat silica surface (dotted line) has isoelectric (zero surface charge) point at pH=2~3. This point shifts to pH=4 for 2.6-nm silica pores

Reduced refractive index in nanopores



Air, n = 1   Bulk water, n = 1.33



Water confined in nanopores shows reduced refractive index/dielectric constant

Significance

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

Biology ⟷ Inorganic Nanostructures
Molecular Modeling ⟷ Molecular Synthesis

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)

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