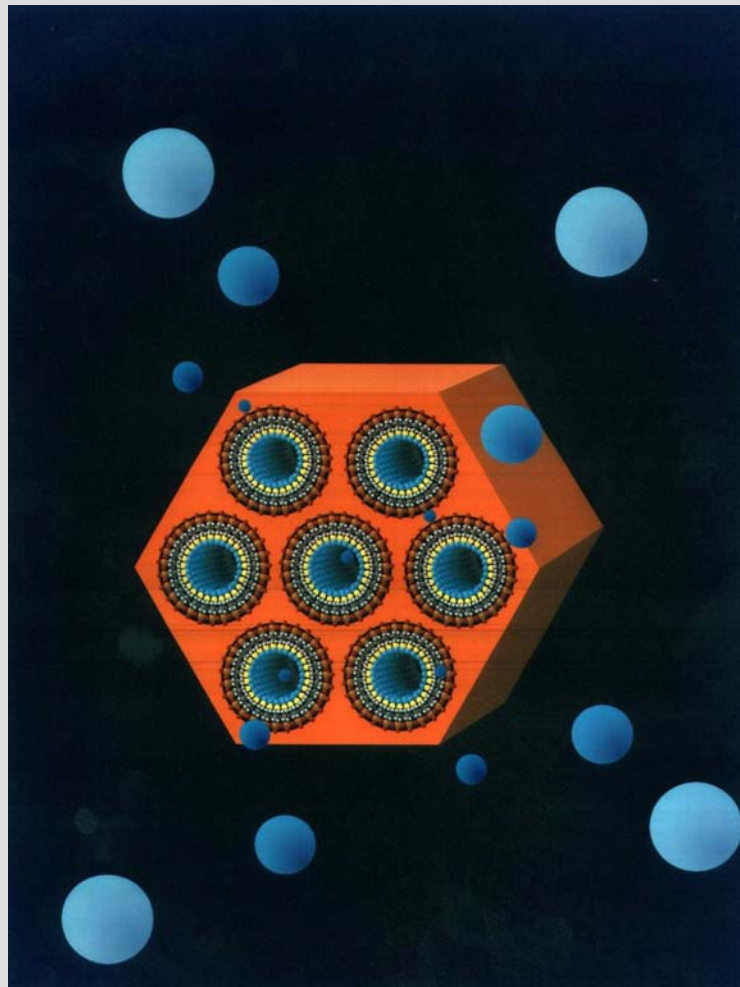


Nanomaterials for Environmental Remediation



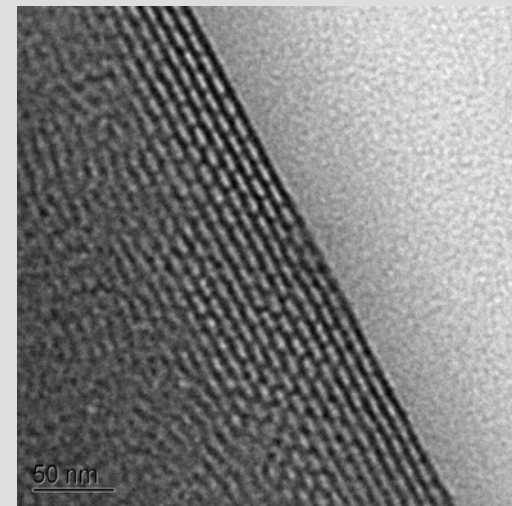
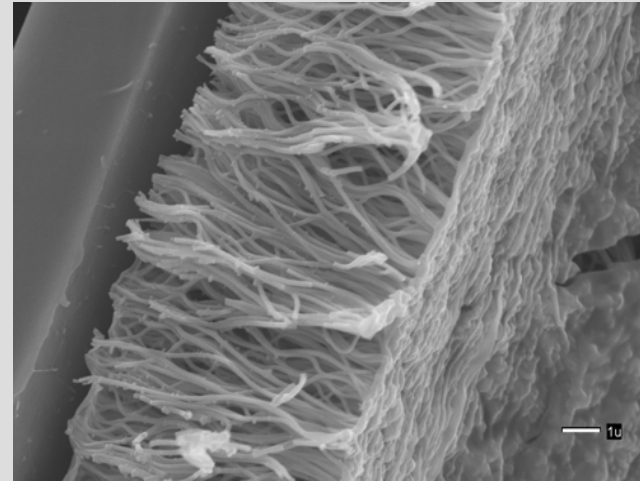
Glen E. Fryxell
Pacific Northwest
National Laboratory
Richland, WA

glen.fryxell@pnl.gov

Advantages of nanomaterials

Nanomaterials provide:

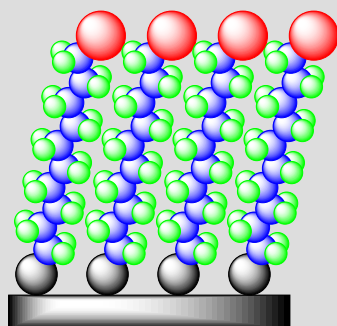
- ▶ High surface area (capacity)
- ▶ Well defined structure
- ▶ High reactivity
- ▶ Easy dispersability
- ▶ Readily tailored for application in different environments
- ▶ Chemistry/materials developed for remediation processes are readily tailored to sensing/detection



SAMMS: Self-Assembled Monolayers on Mesoporous Supports

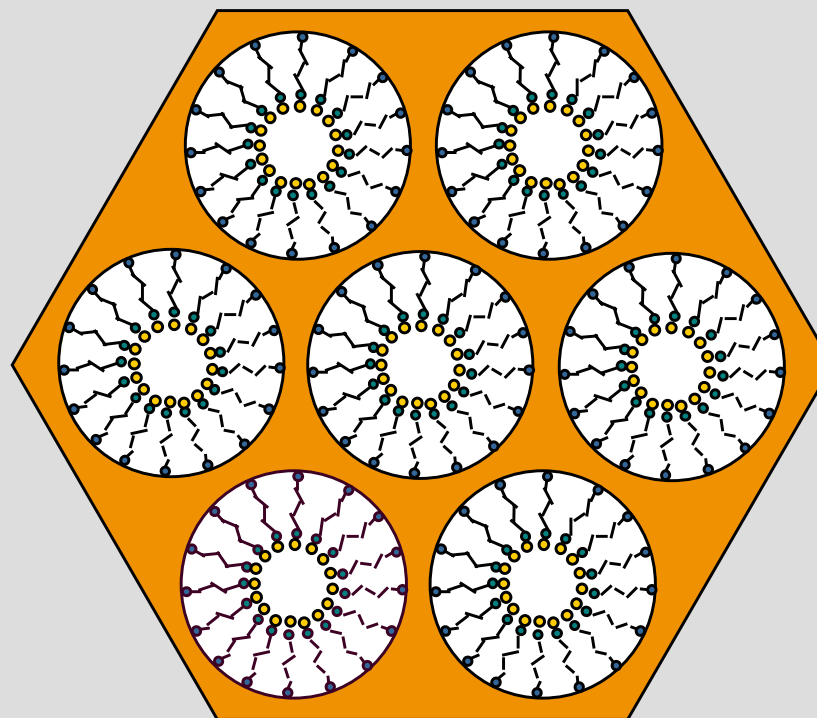
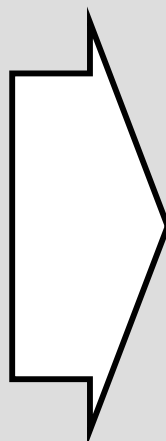
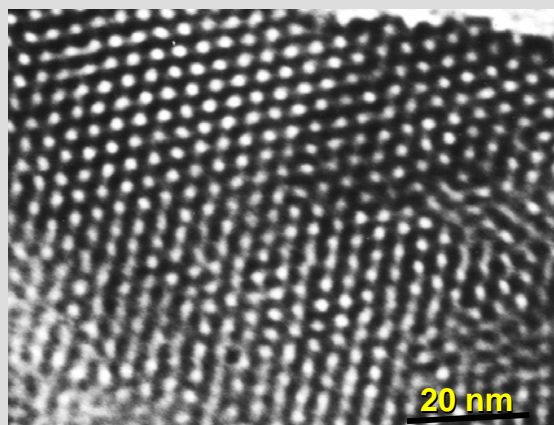


A. Self-assembled monolayers



+

B. Ordered mesoporous oxide

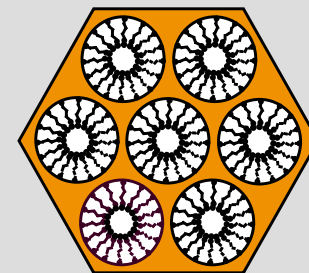


First reported in:

Science 1997, 276, 923-926.

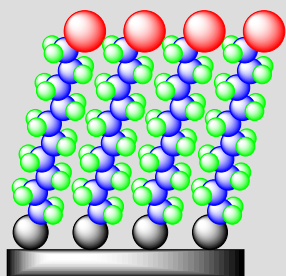
SAMMS in a Nutshell

- Extremely high surface area = high capacity
- Rigid, open pore structure provides for fast sorption kinetics
- Chemical specificity dictated by monolayer interface
- Easily modified for new target species
- Sequestration can be driven either by metal/ligand affinity or by adduct insolubility
- Good chemical and thermal stability
- Easily regenerated/recycled



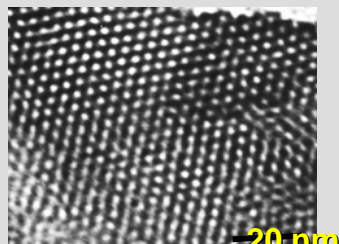
"Designing Surface Chemistry in Mesoporous Silica" in "Adsorption on Silica Surfaces"; pp. 665-687, Marcel-Dekker, 2000.

Functional Nanomaterials for analytical preconcentration



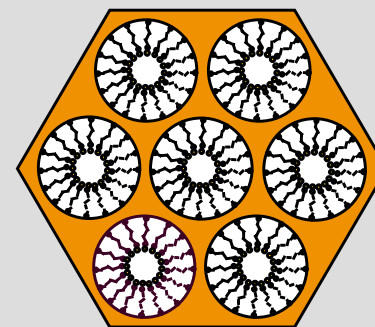
Self-assembled monolayers

- Dense surface coverage
- Chemical specificity

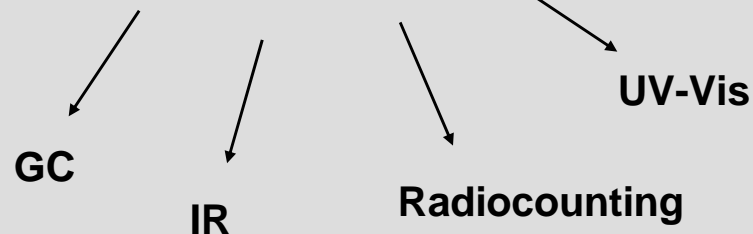


Mesoporous materials

- High surface area
- Rapid sorption kinetics

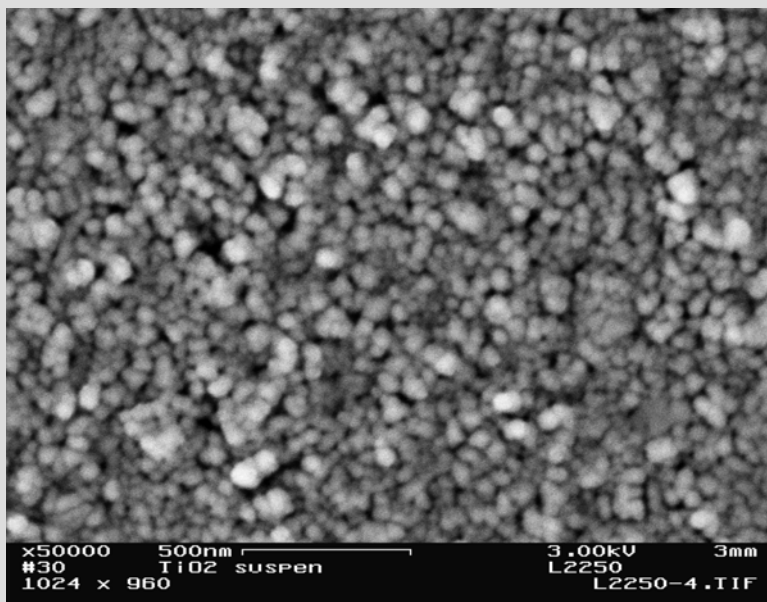


High-performance preconcentrators



“Self-Assembled Monolayers on Mesoporous Supports (SAMMS): Environmental Clean-up and Enhanced Sensing Capability” *Encyclopedia of Nanoscience and Nanotechnology*, Marcel-Dekker, 2004

Functionalized TiO₂ Nanoparticles for Subsurface Injection



Anatase Nanoparticle Injection Tests

An aqueous suspension of anatase (ammonium carboxylate ~ 2 wt %) was successfully injected into a 100 cm long, 20 – 30 mesh sand column (~35% porosity).

The inlet pressure after injection of 3 pore volumes of suspension remained low (<14 psi).

An average of 4 wt % of anatase was uniformly distributed throughout the sand column.

TiNano40™ Characteristics

<i>Surface Area (BET)</i>	51.2 m ² /g
<i>Particle Density</i>	3.88 g/cm ³
<i>Particle Size</i>	40 – 60 nm
<i>TiO₂</i>	99.8%
<i>Impurities</i> (ZrO ₂ , SiO ₂ , Cl, P ₂ O ₅ , ZnO)	0.2%
<i>Crystalline Phase</i>	Anatase

Tc-99 Adsorption Experiment

Adsorbent: Cu-EDA anatase nanoparticles

Contact Solution: Hanford GW spiked with 49.5 pCi/ml of Tc-99

Hanford Ground Water (mg/l)

Ca	49.5
NO ₃	8.6
Mg	14.6
SO ₄	64.7
K	1.7
Si	16.5
Na	13.2
CO ₃	60.8
Cl	16.4
pH	8.3 (SU)
EC	0.47 mS/cm

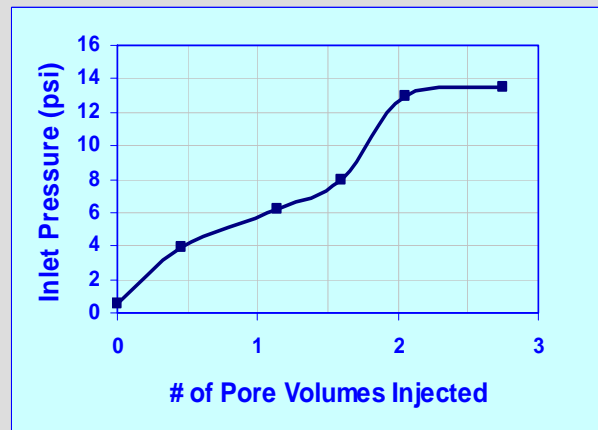
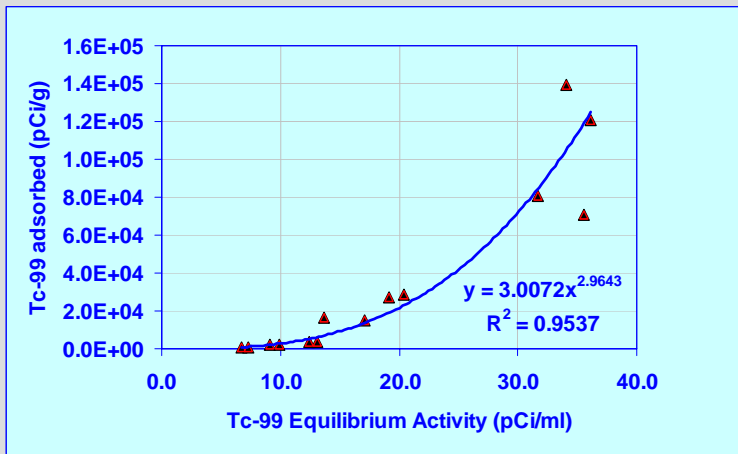
Solution: Solid Ratio (ml/g) :

25, 50, 100, 500, 100, 5000, 10000

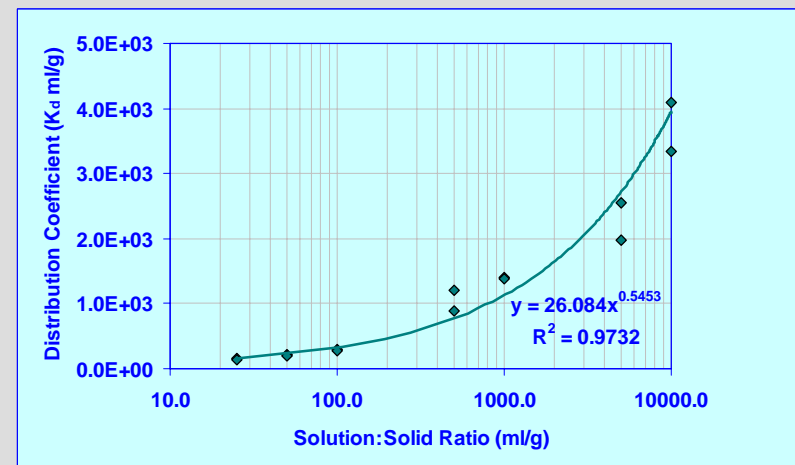
Tc-99 Sequestration by Functionalized TiO₂ Nanoparticles

Tc-99 Adsorption Experiments

Maximum Tc-99 loading: $\sim 1.3 \times 10^5$ pCi/g.
Tc-99 K_d: $1.5 \times 10^2 - 4.0 \times 10^3$ ml/g.



Inlet Pressure Change as a Function of Pore Volume



Summary

Anatase nanoparticles were successfully functionalized with Cu-EDA monolayers.

Cu-EDA anatase selectively adsorbed Tc-99 from spiked Hanford ground water.

Successful injection of an aqueous suspension of anatase nanoparticles into a sand medium was demonstrated.