Development and Advancing Membrane Technologies

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The ‘Nano’ Scale Today and Tomorrow

Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers (US NNI). Novel/new properties as a function of scale.

- Diverse field of material types, applications, instrumentation, etc.

1 TRILLION dollar per year, international industry by 2015 (US NSF).

- Approximately 1000 products worldwide now claim ‘nano’

US - 2012 National Nanotechnology Initiative Budget: $1.7 billion ($18 b 2001-2012)

- $100 million budgeted for EHS R&D in 2012
  - NSF, EPA, NIST, NIH, NIOSH lead the way

EU – FP7 (2007-2013) €3.5 billion ($5.5 billion USD) for nanoscale science and technology.

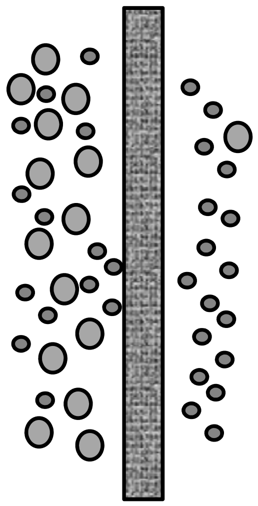
- EU and US agree to cooperate on environmental nanotechnology impacts (EPA, EC 2007 - present).

Membranes in Wastewater/Water Treatment

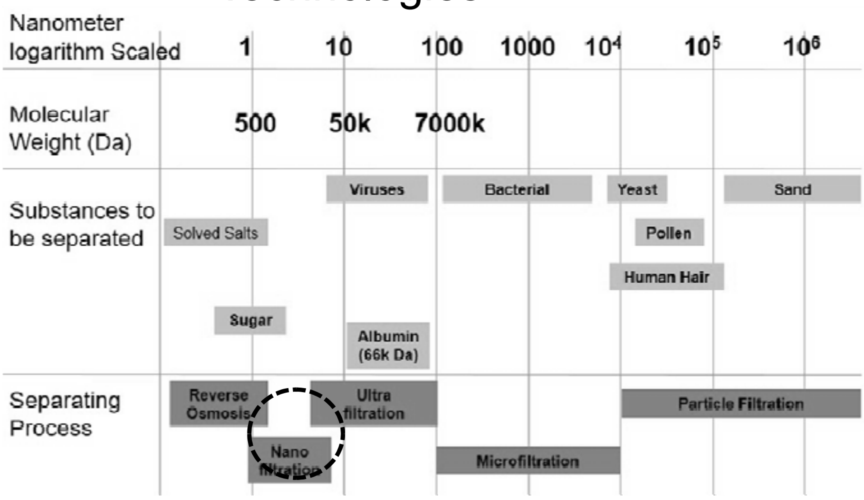
- 1748: Osmosis by French cleric, J. Abbe Nollet
- 1907: Ultrafiltration by Heinrich Bechhold
- 1950: Membrane Desalination by Gerald Hassler
- 1962: Asymmetric cellulose acetate membrane developed by Sidney Loeb and S. Sourirajan at UCLA
- 1963 : beginning of practical membrane applications
- 1971: Aromatic polyamide membrane patented by Richter-Hoehn and assigned to DuPont
- 1987: microfiltration membranes introduced to the municipal water treatment market
- Present: $5.54 billion market in 2012 and estimated to reach $12.07 billion in 2020 (by Frost & Sullivan).

Membrane Technologies

Schematic Diagram of Membrane



Cut-offs for Filtration Technologies



Performance: Permeability = $\frac{Q}{t*S*P}$ vs. Selectivity (Rejection)= $1-\frac{C_{out}}{C_{in}}$

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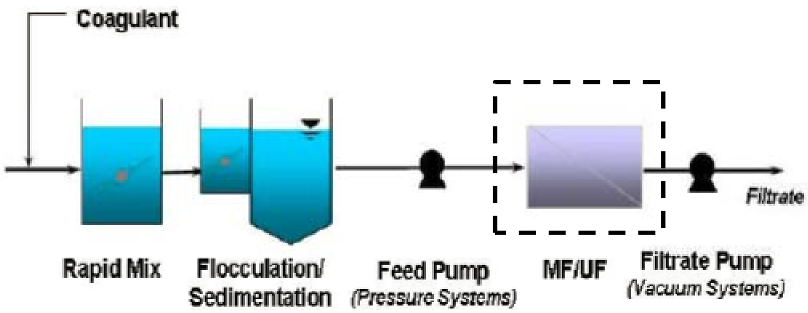
Microfiltration/Ultrafiltration Membrane



Pore size:

- MF: 0.1- 10 um
- UF: 10-100 nm

Pretreatment processes (for such as, Reverse Osmosis)

Materials: organic (polysulfone, polypropylene, cellulose acetate, etc.), inorganic (ceramic, porous alumina, etc.).

Removal of particulate and microbial contaminants

- Particulates: suspended solids, turbidity, colloids, bacteria, protozoan cysts, and viruses (UF)
- Inorganics: phosphorus, hardness and metals (with suitable pretreatment)
- Limited dissolved organics

source: Water Research Foundation, 2009

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Reverse Osmosis Membrane

Ashkelon SWRO Plant, Israel

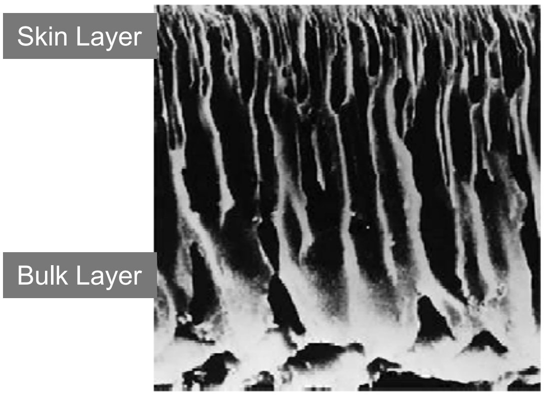
Semipermeable Membrane

- < 1 nm (salt ions)
- High pressure (energy cost)

For 2011, RO was used in 66% of installed desalination capacity (44.5 of 67.4 Mm^3/day), and nearly all new plants (International Desalination Association).

Common Commercial Membranes

Acetate Cellulose Membrane

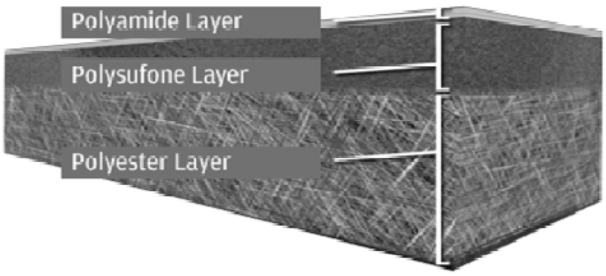


Structurally dissimilar

- Low purchase cost.
- Tolerant of chlorine in feed water.

- Poor rejection
- Higher pressures and costs

Thin Film Composite (TFC) Membrane



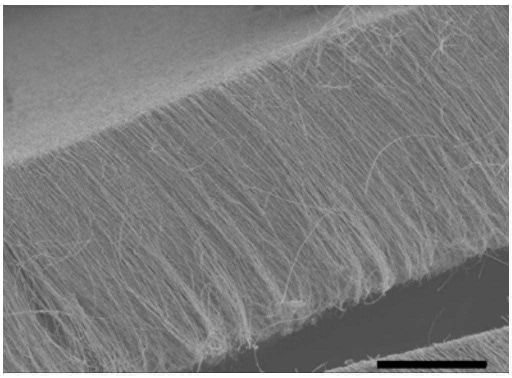
Dissimilar materials

- Excellent membrane flux and lower pressures.
- Superior rejection of salts and organics.
- Excellent stability and durability.

- Limited tolerance to chlorine

Image source: Fishersci, auxiaqua

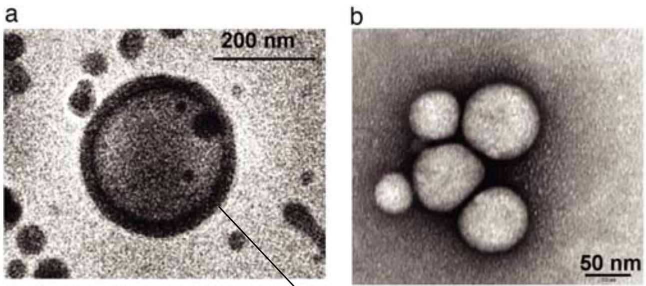
Advanced Nanotech-enabled Membranes



Vertically Aligned CNTs

water permeation through CNTs occurred at a rate **3-5 orders** of magnitude higher (faster) than predicated by the Hagen-Poiseuille equation due to violation of no-slip boundary conditions

Hinds et al., Science, 2004



Biomimetic Membranes

large enhancement in water productivity (up to **800 times**), as compared to that of pure polymer

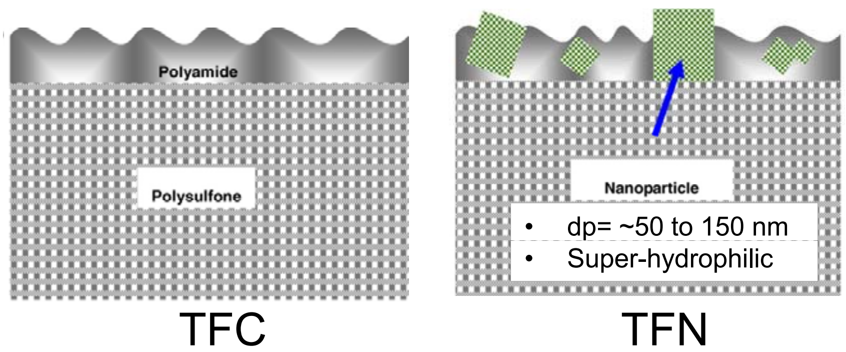
Kumar, et al., PNAS,2007

triblock-polymer vesicles incorporated with the bacterial water channel protein Aquaporin Z

Economic Scale-up Production ?!

Incorporation of Nanomaterials

- Thin Film Nanocomposite (TFN) Membrane: incorporation of nanoparticles within the polymeric film during interfacial condensation



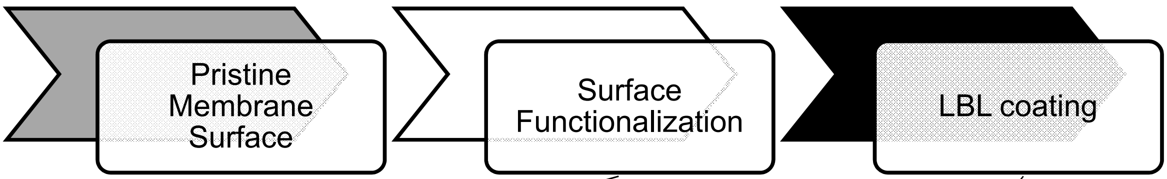
- Contact Angle: decreased from 70 ° to 40 °
- Permeability can be **doubled**
- Solute rejection remains constant (> 90% for PEG 200, Mg^{2+} , and Na^{+})

- Changed polymer chemistry might affect the membrane performance
- Sacrificed surface area of nanoparticles buried in bulk phase

Jeong et al., 2007

Membrane Surface Coating Technologies

Layer-by-layer (LBL) coatings: based on electrostatic interactions between oppositely charged polyelectrolyte layers



- Chemical Degradation: e.g. plasma treatment
- Chemical Addition: polymer blends

- *in situ* nanomaterial synthesis
- binding of prefabricated nanomaterials: electrostatic, covalent

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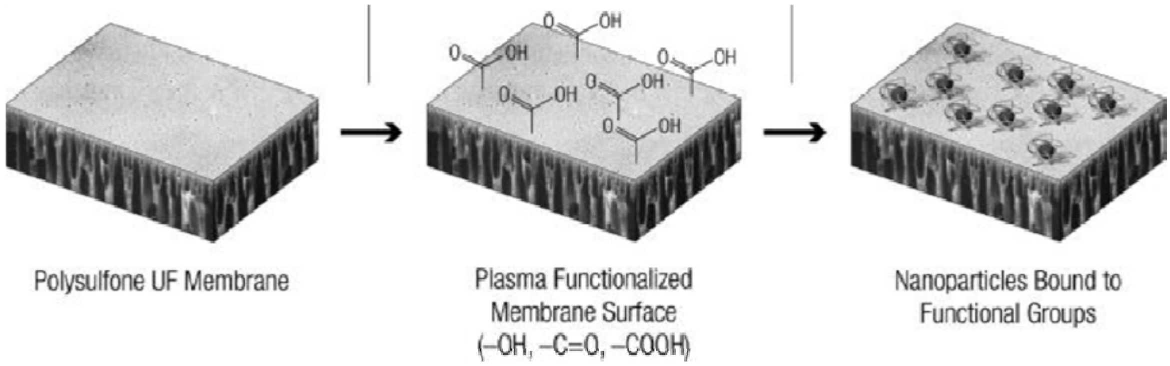
Example 1: PSf Membrane Functionalized by Ag NP



- MWCO=50 kDa
- P = 75 L/m^2·h·bar

- Increase of oxygenated functional groups (thus wettability)
- Optimal treatment time: 60 s (after which rejection decreases)
- P = ~130 L/m^2·h·bar

- Surface Charge: - → +
- Rejection restores
- P = ~ 30 L/m^2·h·bar
- Antibacterial: inactivation rate of 94%

Mauter et al., 2011

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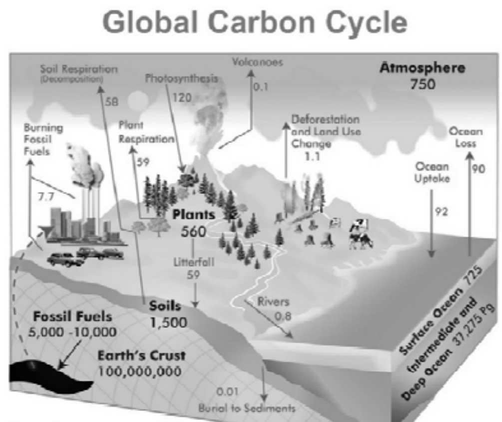
Carbon Nanomaterials



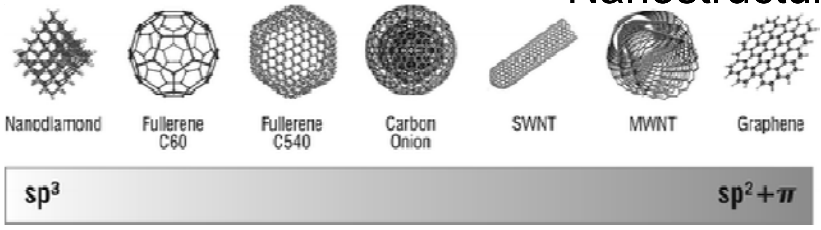
Source:
NASA/GLOBE Program

Carbon $>10^9$ GT

Most Well-known structures

- Amorphous Carbon: charcoal, activated carbon., etc
- Graphite
- Diamond

Newly Discovered Nanostructures



Source: Mauter and Elimelech, ES&T, 2008

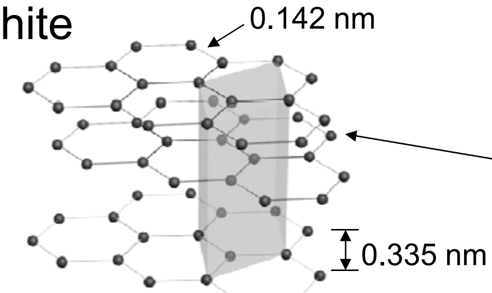
C60: *Kroto, et al., Nature, 1985*

CNT: *Iijima, Nature, 1991*

Graphene*: Novoselov, et al., Science, 2004*

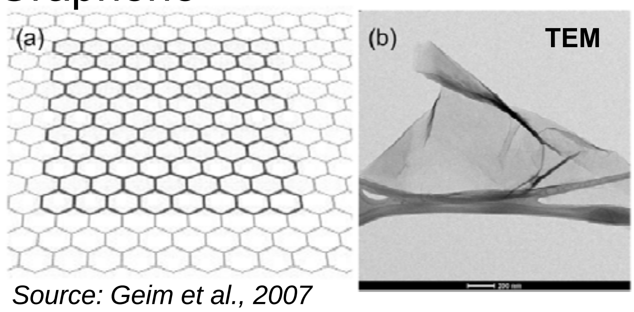
Graphene: Structure-Properties

Graphite



Source: Wikipedia commons

Graphene



Source: Geim et al., 2007

Structures

One atom-thick layer of (free-standing) graphite, basic structural element of other carbon structures

Carbon atoms are densely packed in a regular sp^2-bonded hexagonal pattern

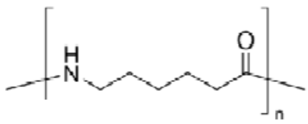
Properties

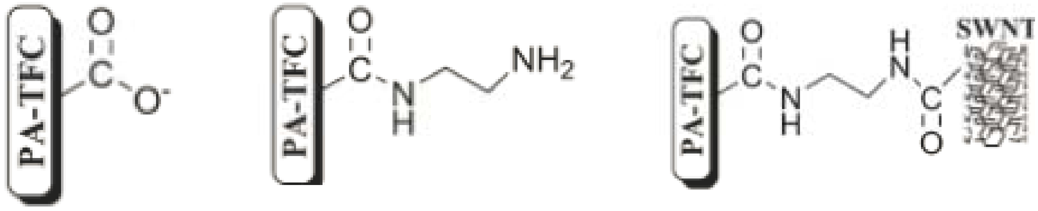
- Remarkable mechanical property
- High crystal quality
- Exceptional electronic quality
- Extreme specific surface area
- Easiness to be functionalized

Example 2: TFC Membrane Functionalized by SWCNT

PSf membrane + interfacial polymerization = TFC-PA

Polyamide (PA)



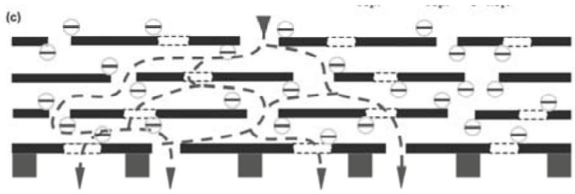


- Contacting angle (wettability) did not change much
- Water permeability increased slightly
- Bacterial inactivation: ~60%

Tiraferri et al., 2011

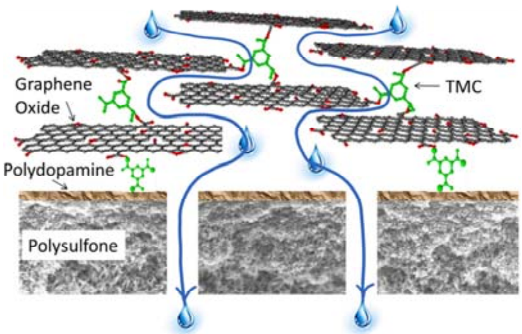
Graphene Oxide Membranes

Ultrathin GO membranes



Han et al., Adv. Funct. Mat., 2013

- Made by vacuum filtration
- Q = 21.8 L/(m^2·h · bar)
- Rejection of organic dyes (MB, > 99%)
- Rejection of ion salts (Na^+, Mg^{2+}, ~ 20 - 60%)



Hu and Mi, ES&T, 2013

- Made by layer by layer deposition
- Q = 8 - 27.6 L/(m^2·h · bar)
- Rejection of monovalent and divalent salts (6−46%)
- Rejection of MB (46−66%)
- Rejection of Rhodamine-WT (93−95%)

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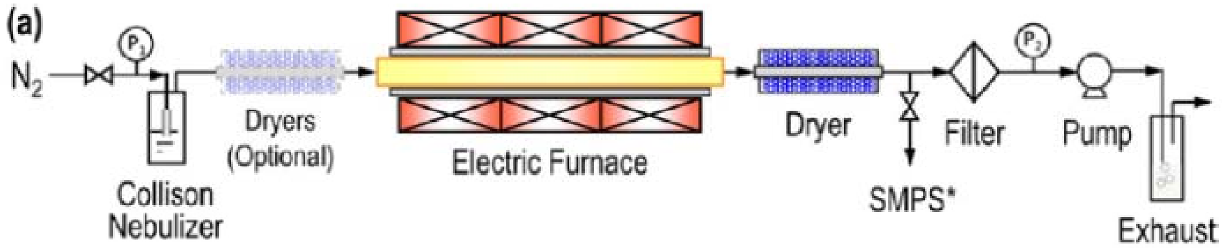
Aerosol Synthesis

Furnace Aerosol Reactor (FuAR)



Experimental

Parameters	Conditions
Pressure (flow rate)	8-30 psi
Furnace Temperature	RT.-1000 ^{o}C
Diffusion Dryers	0-2
Precursor	Concentration (0-1 mg/mL)
	Mass ratios: 0%- 20%

Material Characterization

Online:
Scanning Mobility Particle Sizer (SMPS)
Aerosol Particle Sizer (APS)

Offline:
Transmission Electron Microscopy (TEM)
Scanning Electron Microscopy (SEM)
Dynamic Light Scattering (DLS)
UV-vis

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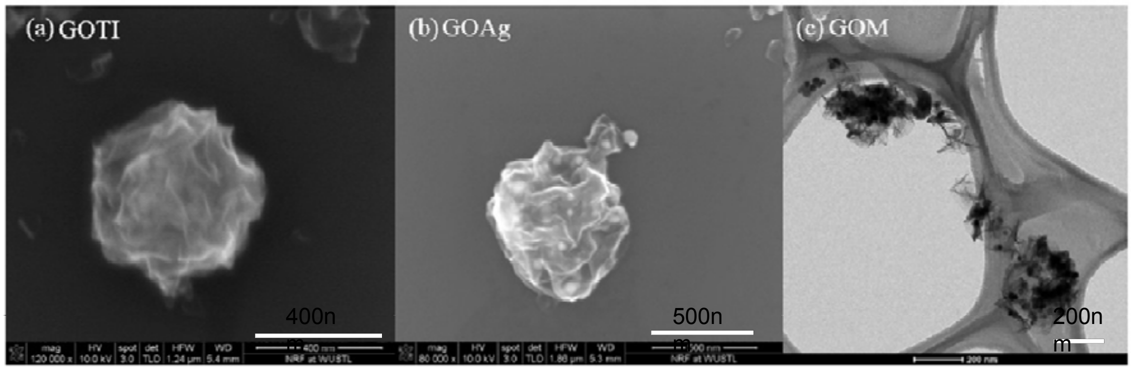
Binary CGO Nanocomposites

Adjust the
Precursor

Pure GO

GO+TiO_2



Types of CGO nanocomposites with different cargos

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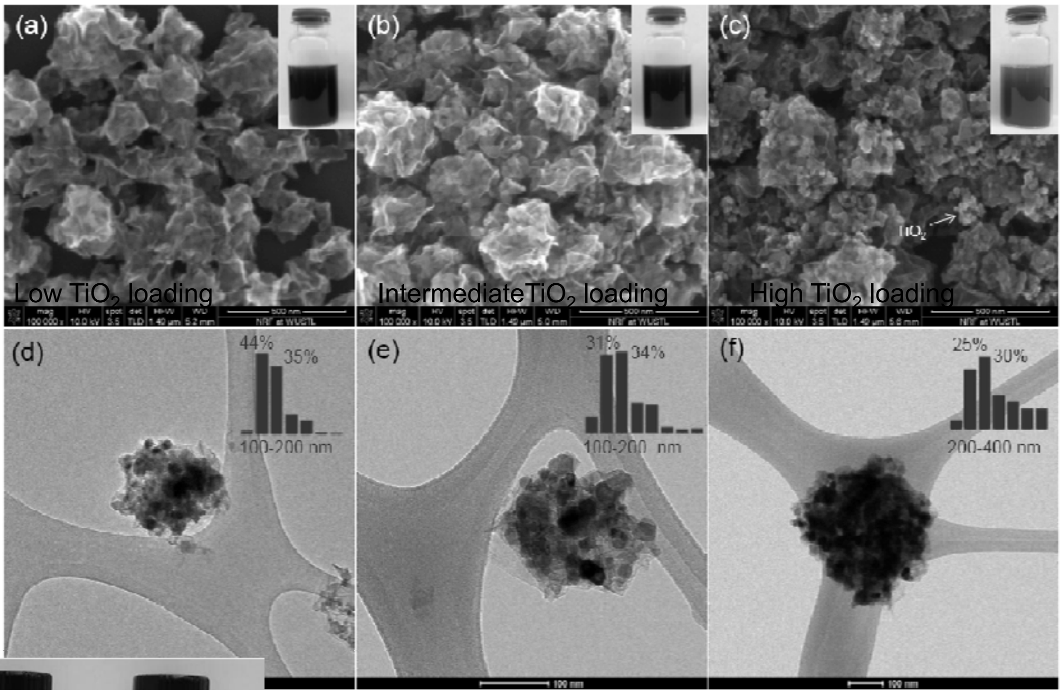
Ternary GOTIM Nanocomposites



- Highly water-stable
- Size and functionality could be tuned by adjusting the TiO_2/magnetite ratio
- Capable of being recovered under low magnetic field

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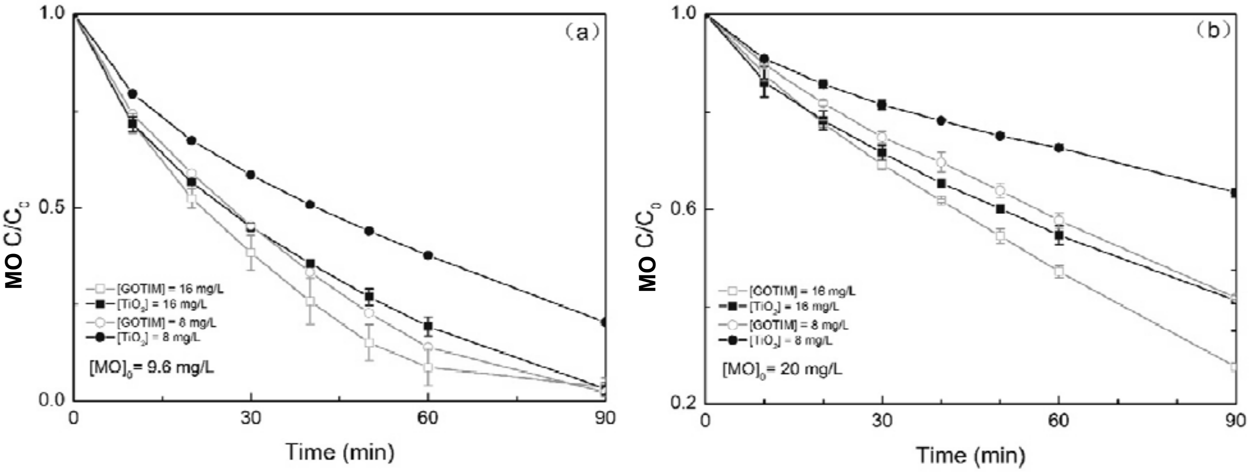
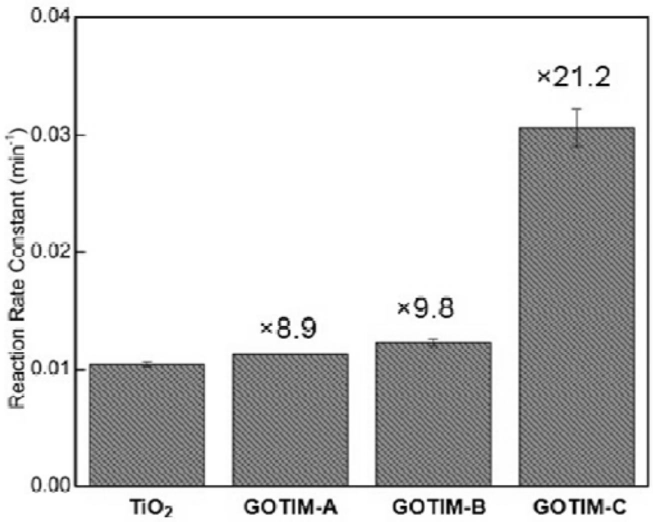
Photocatalytic Performance Enhancement



•GOTIM has improved photocatalytic performance compared to bare TiO_2, which was due to possible increases in dye adsorption, enhanced light absorption range and efficient charge separation and transfer *(Zhang et al., ACS Nano, 2010)*

•Agreeable fitting of pseudo first order kinetic parameters suggested a pseudo first order reaction

Photocatalytic Enhancement Factor



- The enhancement, normalized based on mass ratios, could reach as high as > 20 times, compared with bare TiO_2.
- Increased light intensity could enhance the photocatalytic activity greatly; and GOTIM is more sensitive to light intensity than is TiO_2

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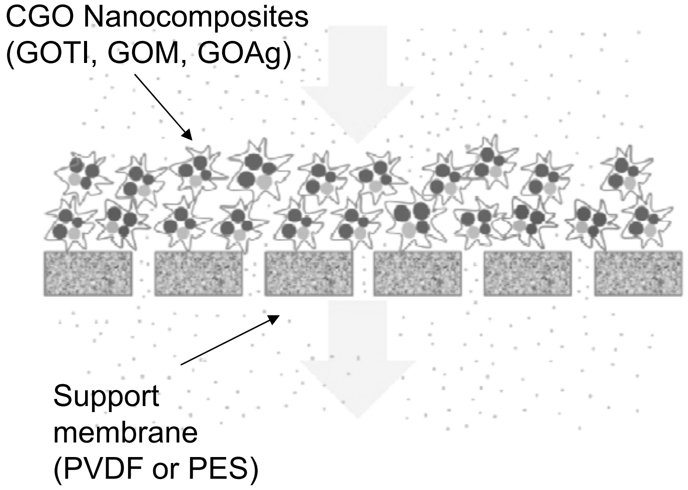
Fabrication of CGO Membrane

Membrane Fabrication:
vacuum filtration



Characterization:

- Morphology: SEM, AFM.
- Hydrophilicity: Contacting Angle
- Surface Chemistry: SEM-EDS, laser Raman spectroscopy imaging and XPS
- Surface pore size: SEM image analysis by ImageJ

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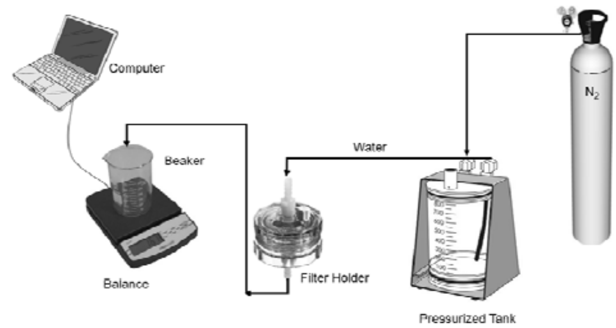
Filtration and Photocatalytic Reaction

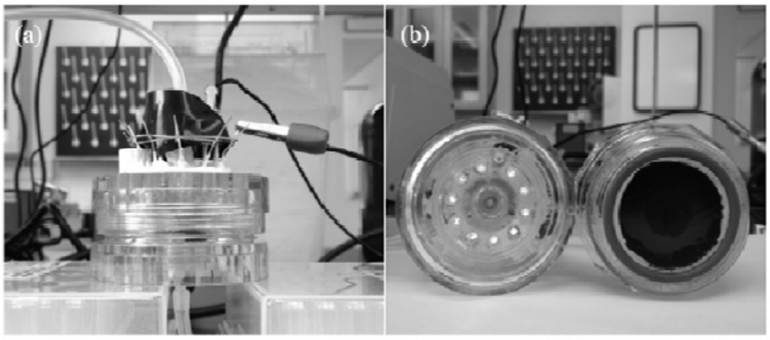
Filtration Set-up



Parameters	Conditions	Measurement
Pressure	1-2 bar	
Organic pollutants	methyl orange (7.5 mg/L) and bovine serum albumin (10 mg/L)	UV-vis
Ion salts	NaCl (20 mM) and $MgCl_2$ (10 mM)	Conductivity Meter

In addition to MO and BSA, molecular weight cut-off (MWCO) analysis:
six polyethylene oxide solutions of increasing molecular weight (4, 10, 35, 50, 95, and 203 kg/mol, 10 mg/L)

Photo-reactivity



Parameters	Conditions
Flow rate	0.1-2 ml/min
Pollutant	methyl orange (7.5 mg/L)

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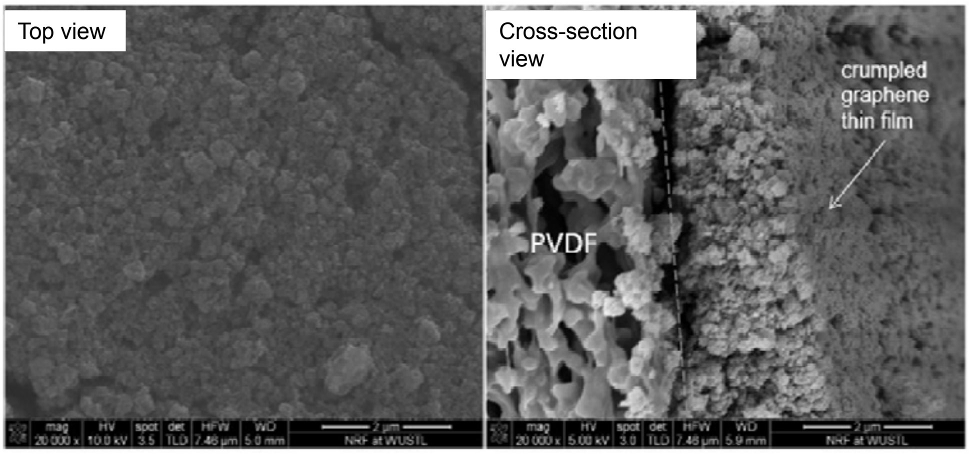
GOTIM Membrane



m = 4 mg

Quasi-spherical GOTIM nanocomposites ranging from 200 to 400 nm packed together and formed the crumpled graphene thin film with a depth of ~ 2.8 um.

Q = 2685±225 $L/(m^2 \cdot h \cdot bar)$

MO adsorption: ~ 17 mg/g

MO rejection: very low

Reaction = 0.0011 min^{-1}

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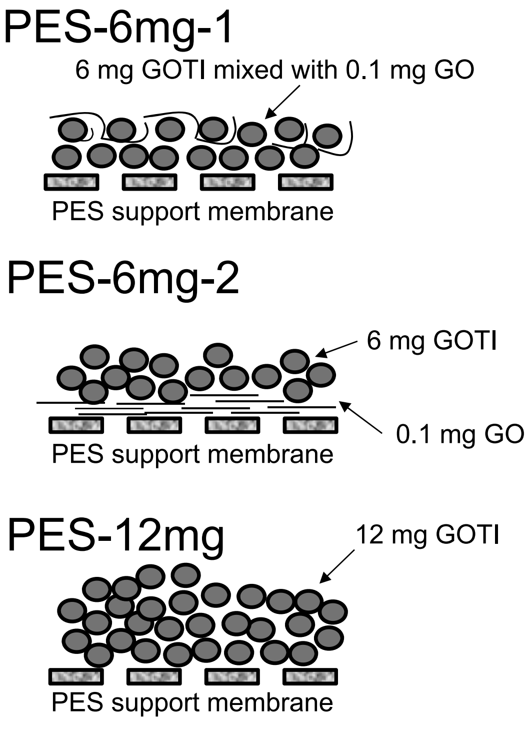
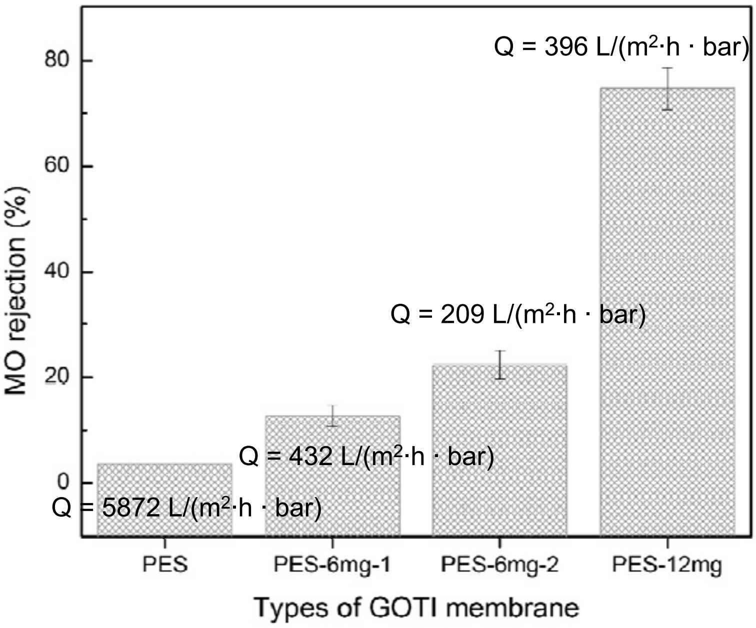
GOTI Membrane Flux and Rejection





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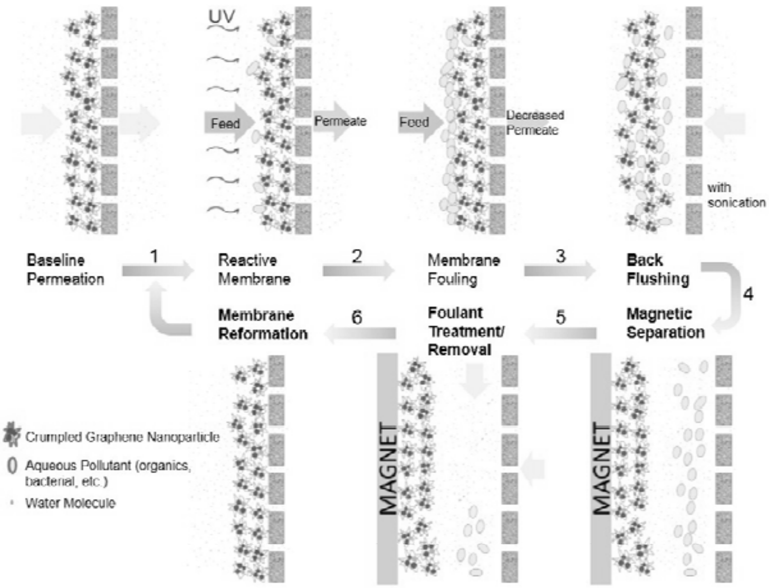
GOM Membrane Reformation Strategy

Membrane Reformation Demonstration



Step 1: Membrane Fouling

- 500 mg/L bovine serum albumin (BSA) fouling for 20 min.
- Q ~ 4700 L· m^{-2}·bar^{-1}· h^{-1} to ~ 600 L· m^{-2}·bar^{-1}· h^{-1}

Step 2: CGO off membrane

- back flushed and sonicated apart from the PVDF membrane surface

Step 3: Cleaning

- mildly by adding small quantity of HCl

Step 4: Magnetic Separation

- separated from the cleaning solution by a low field magnet

Step 5: Reformation

- reform via vacuum filtration

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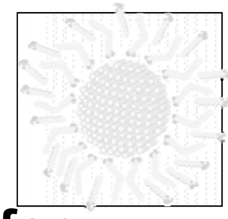
Magnetite Thin Film Case Study



Utilize Nanocrystaline Magnetite (nMAG) for Applications in Uranium Removal and Detection

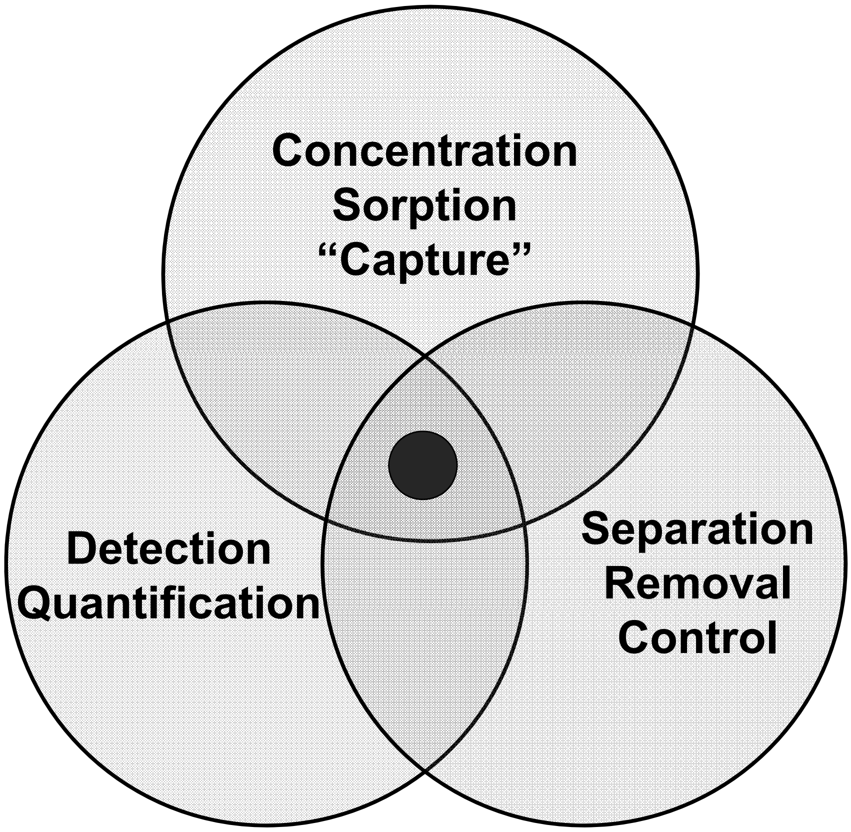
- nMAG Water Stabilization
- nMAG-Uranium Sorption
- Alpha Particle Counting (Advantage)

Project Goal

Materials based, low energy, field capable, trace uranium detection and quantification

What?? No ICP-MS Available??

"Sensing" Material Optimization



Approach

Engineer magnetite based materials (nMAG) for:

High aqueous stability and surface area

- Maintain favorable surface chemistry
- Avoid aggregation (available surface)

Maintaining magnetic properties (separation)

- Control of materials with low magnetic fields (<1.3T)

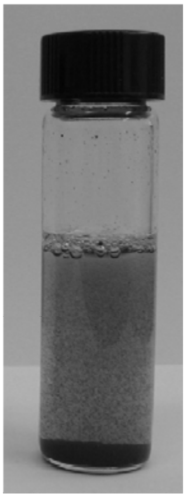
Minimize self (particle) shielding for alpha particle counting (i.e. uranium detection via radiation)

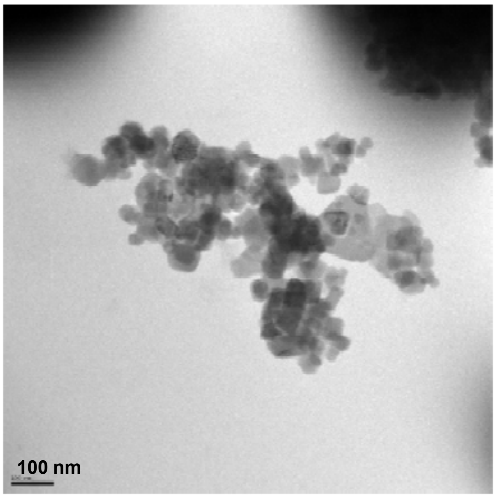
- Thin, homogenous film formations are ideal!!
- Ease of formation/synthesis needed

Advanced Applications:
Critical Issue: (Nano)magnetite

Commercial (Sigma Aldrich) nano-oxides vs. Research grade

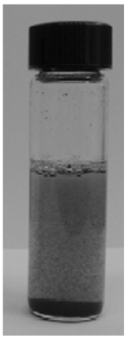
- **Agglomerated in water→ lower net surface area**
- **Larger (nano)particles → lower net sorption**
- **Large size distribution(s) → limited optimization**

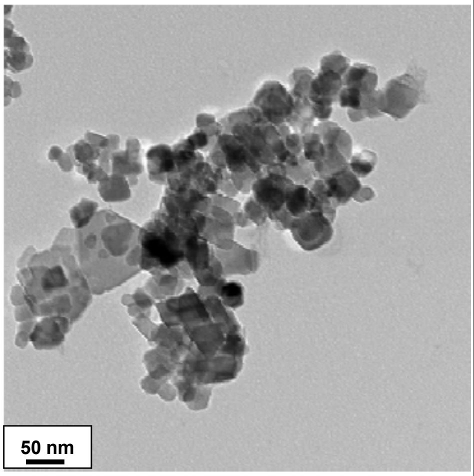




Nanoscale Magnetite Platform
A Closer Look

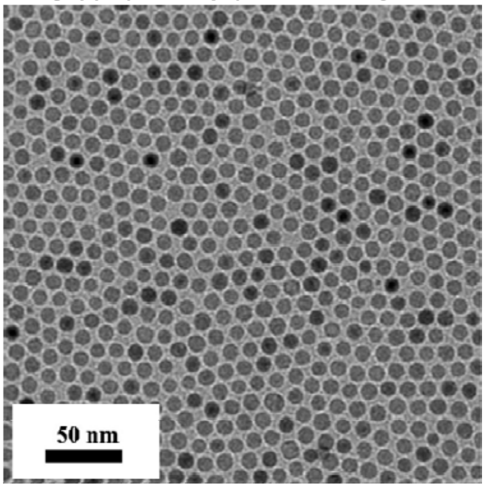
Commercial nMAG

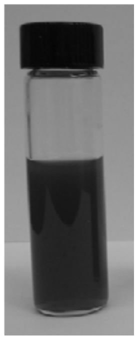




Surface area: 43.67 m^2/g

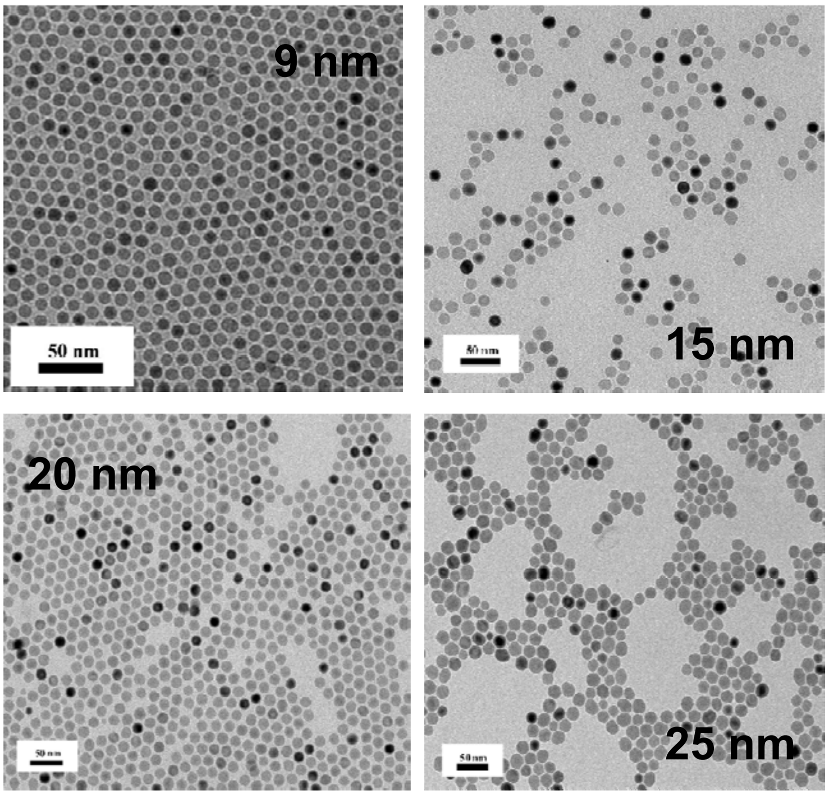
Oleic Acid Stabilized nMAG





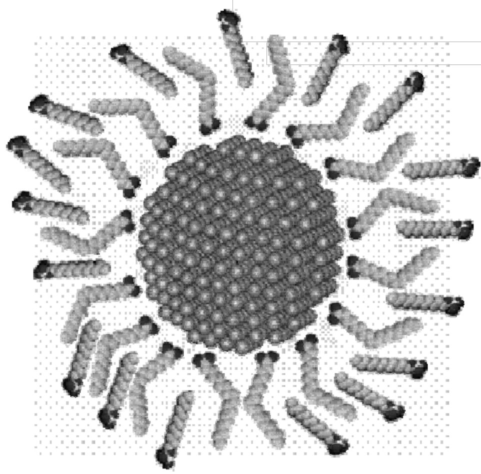
99 m^2/g

Particle Size Control



Critical Issue 2: Aqueous Stabilization

- Relatively stable dispersions
- Available detergents work well
- Organic Acids are better..
- Maintain Magnetic Properties



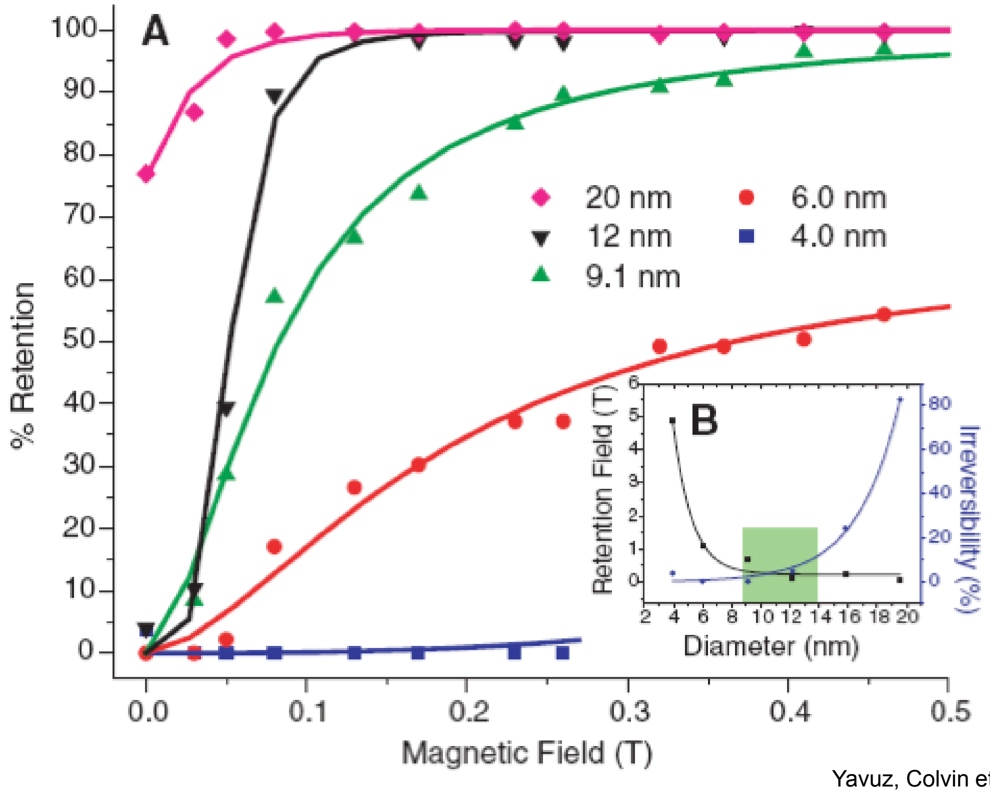
Oleic Acid Bilayer Stabilization

Oleic acid is a common 18-C mono-unsaturated fatty acid (carboxylic acid head group)

Yu, Colvin et al., Chem Comm.; Yavuz, Colvin et al., Science

Critical Issue 3: Separation

Why 8-12 nm?



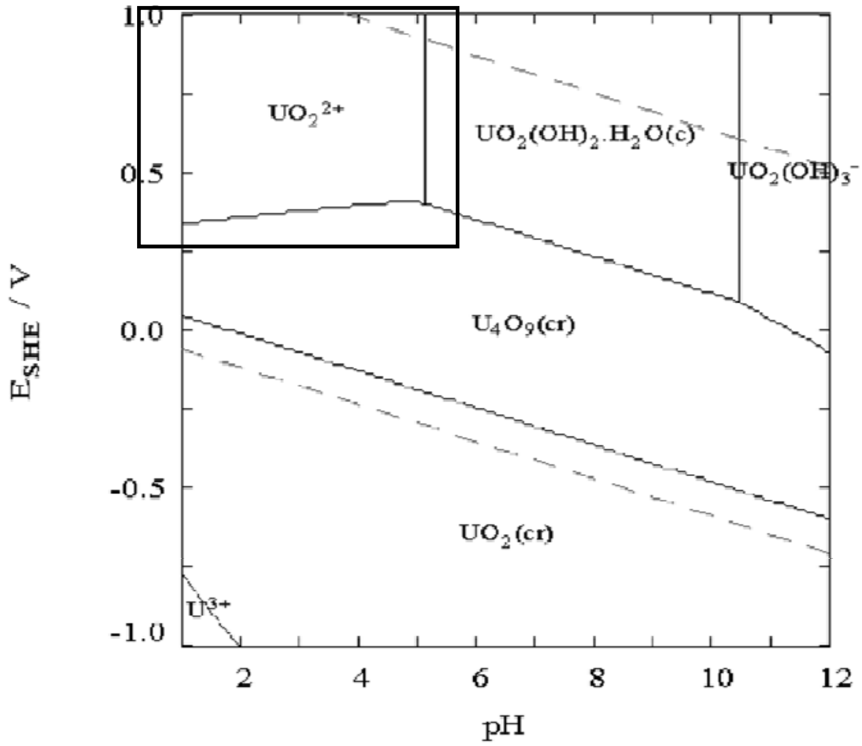
Yavuz, Colvin et al. Science 2006

12 nm nMAG Separation

Material	Seperation	Percent nMAG Removal
Commercial	20 nm Filter	99.9%
Igepal® CO-630	20 nm Filter	99.6%
Oleic Acid	20 nm Filter	98.9%
Commercial	Magnetic	99.9%
Igepal® CO-630	Magnetic	95.3%
Oleic Acid	Magnetic	93.3%

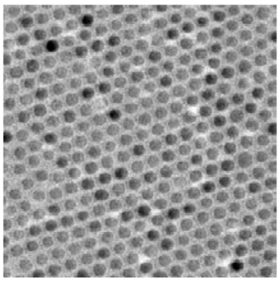
8 hour passive magnetic separation time, neodymium magnet (ca. 1 T); 50 mL reaction tube with a 4 cm radius. Filtration done via aluminum oxide filter membrane (Anopore, Whatman)

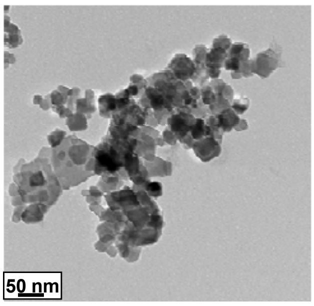
Uranyl - Target Soluble Species

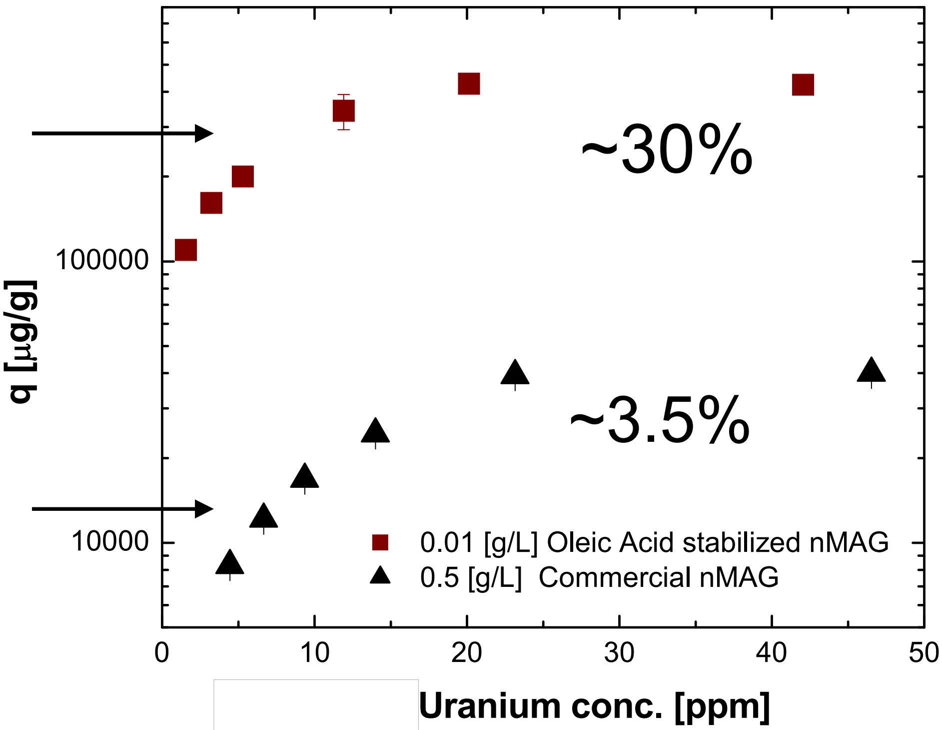


Simple U Pourbaix diagram

Uranyl - nMAG Sorption

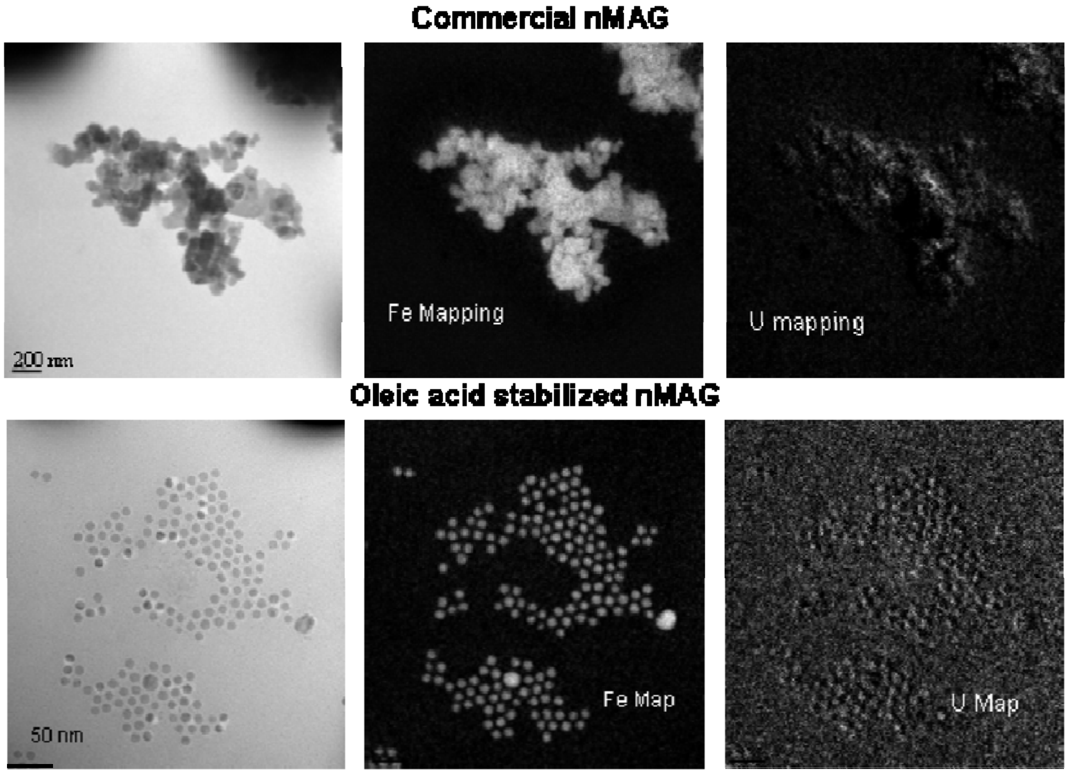




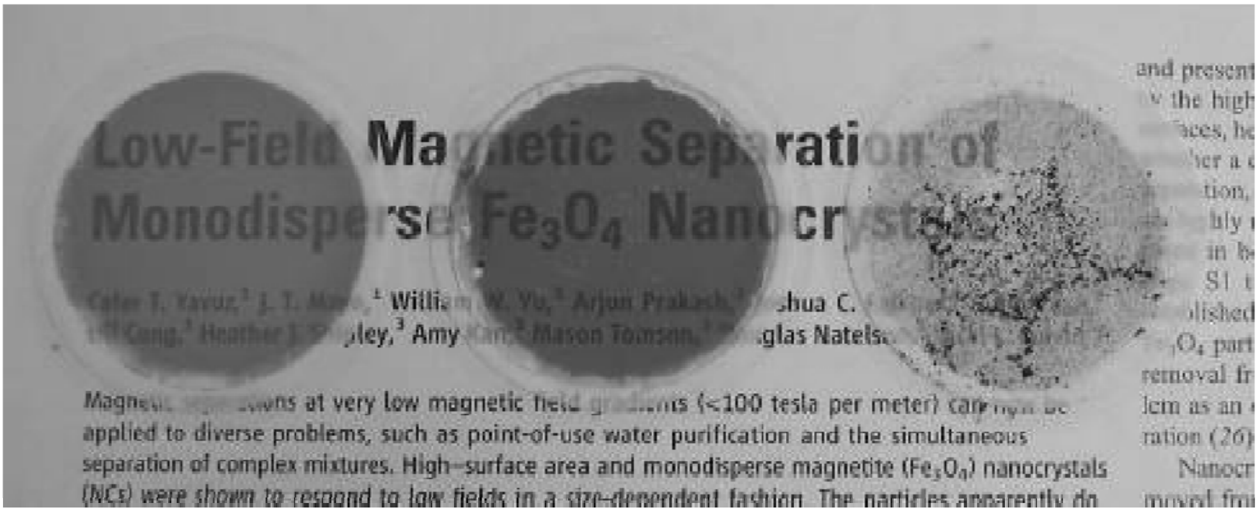


pH 5, DI Water

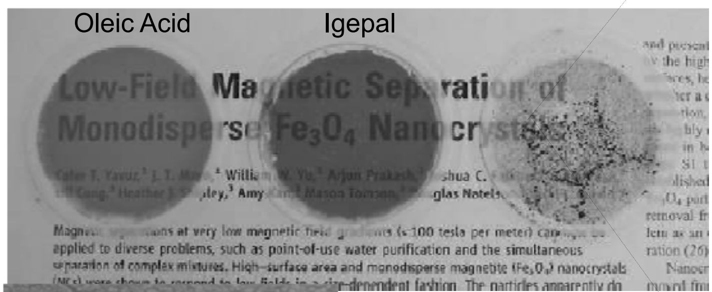
U – nMAG: Sorption: FEG-TEM

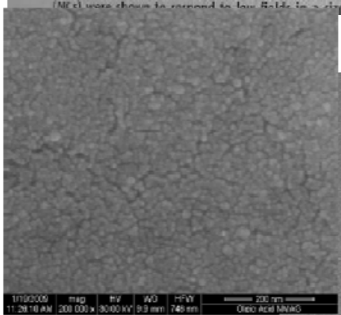


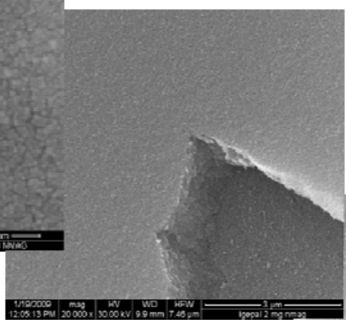
Critical Issue 4: Thin Film Formation

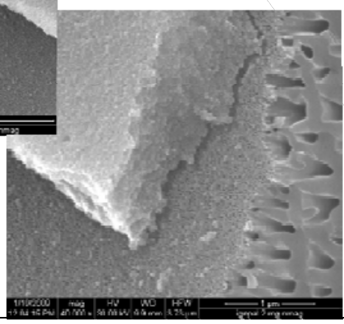


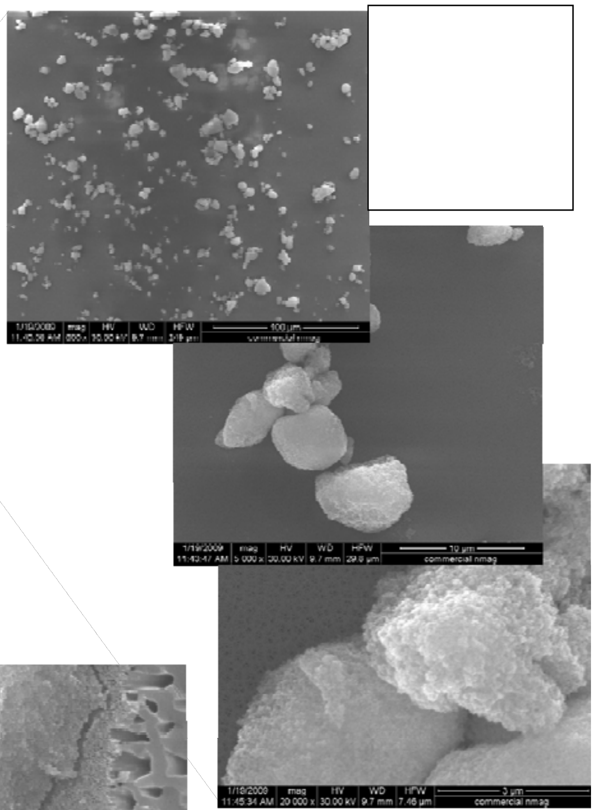
Film Formations





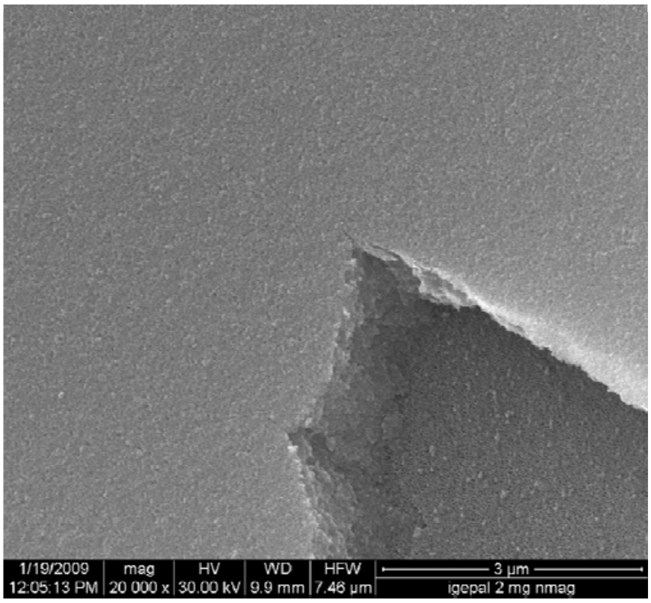




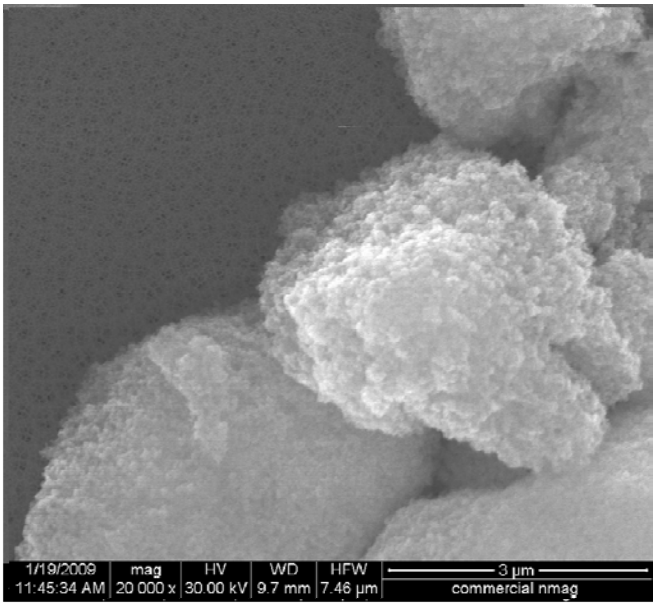


Film of nanoscale magnetite (12 nm) stabilized in water with oleic acid bilayer.

Deposition Comparison

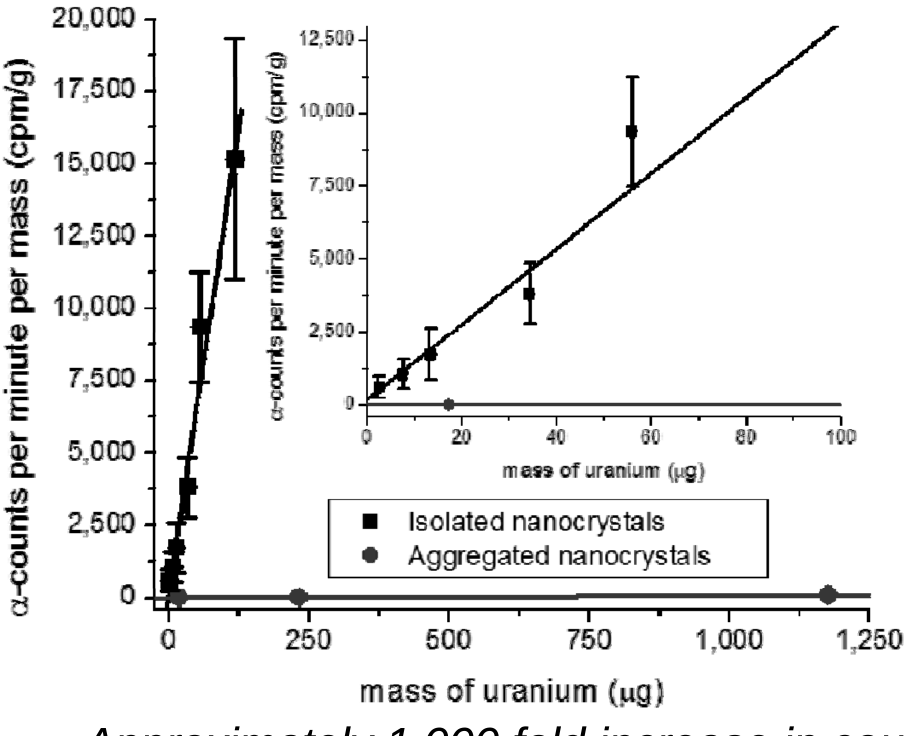


Surface Stabilized nMAG



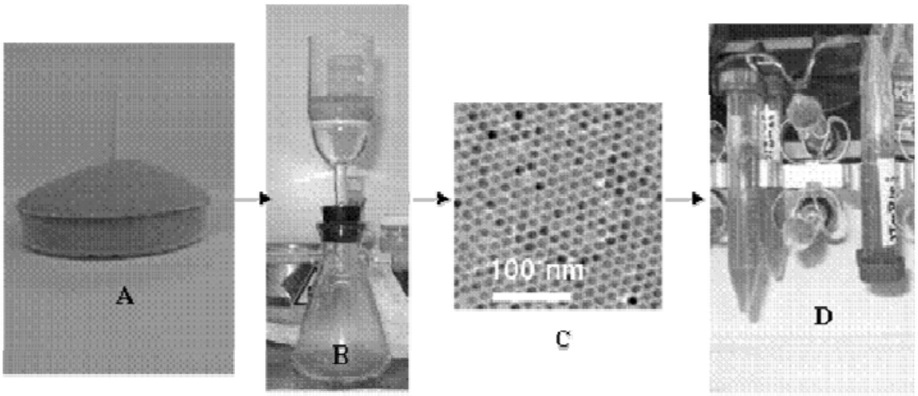
Commercial Available
Nanoscale Magnetite

Alpha Particle Counting Advantage



Approximately 1,000 fold increase in counts observed per mass uranium (normalized)

Combined Process Benefit



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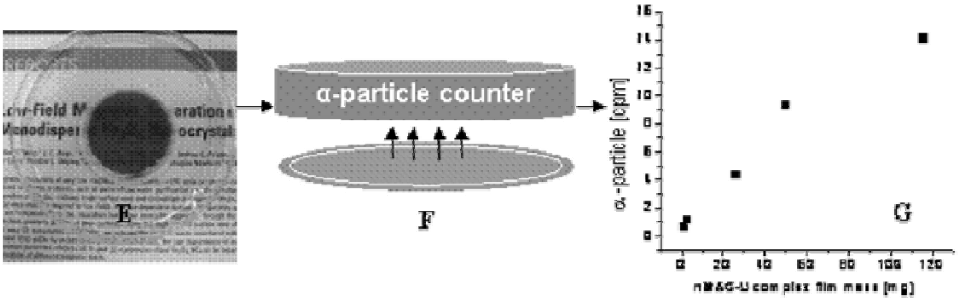

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Questions