Polymeric and Inorganic Nanoparticles for Environmental Applications

Ju-Young Kim
Ph.D. / Associate Prof.
Department of Advanced Materials Engineering
Kangwon National University, Samcheok, Kangwon 245-711, S.Korea

Nano Technology + Environmental Technology

"Nanoparticles"

Environmental Pollution Monitoring

: Nanosensor

- Ag, Au, Pd, SnO_2
- ZnO_2, WO_3, TiO_2
- CdSe
- Carbon Nano Tube (CNT)

Removal of Environmental Pollutants

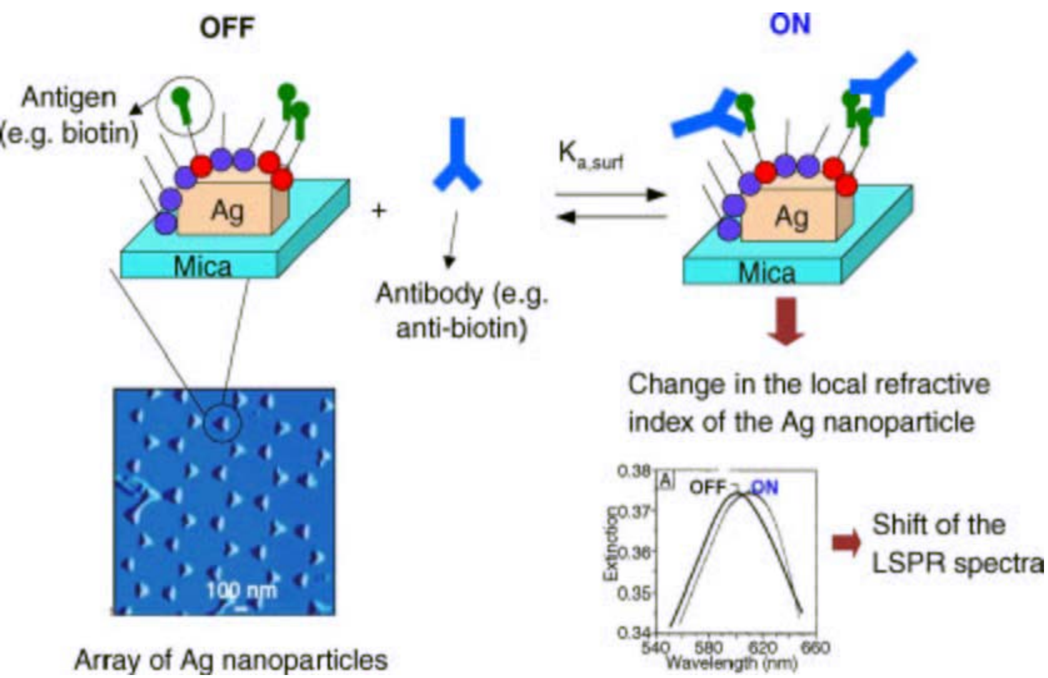
- Magnetic Nanoparticles
- TiO_2 Nanoparticles
- Polymeric Nanoparticles

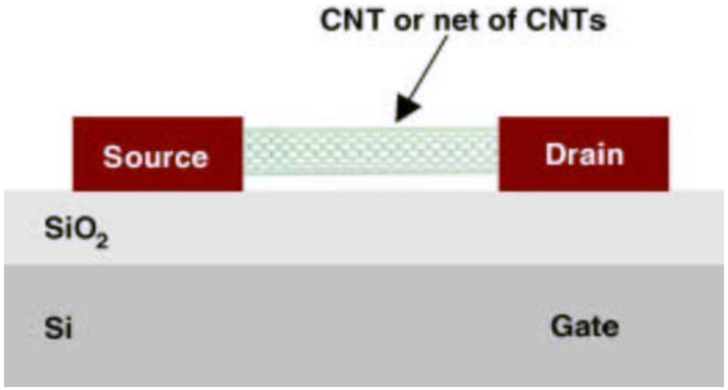
Environmental Friendly Energy Systems

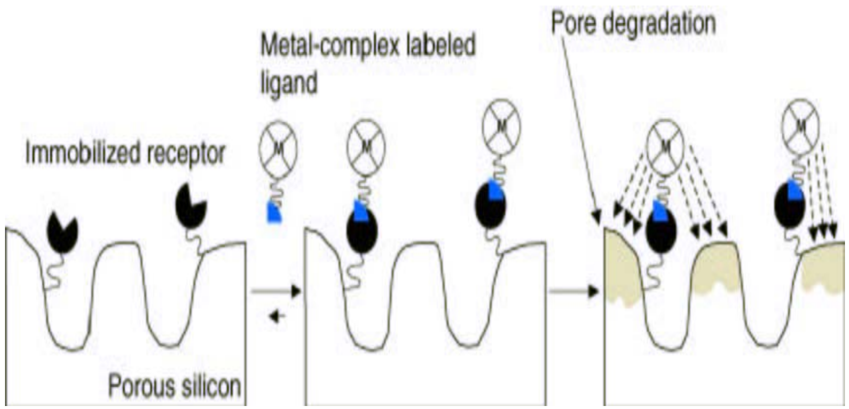
: Fuel Cell, Li-battery Solar Cell

- CNT
- Clay Nanoparticles
- Silica Nanoparticles

Nanosensors for Environmental Monitoring





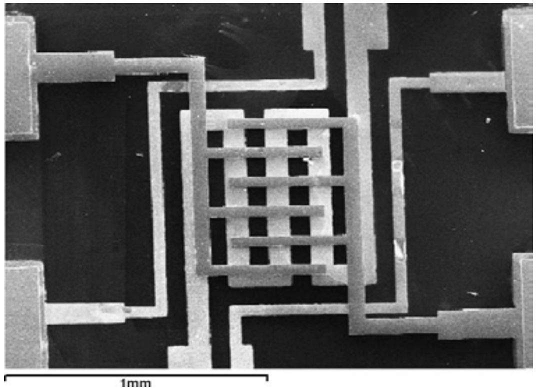


Inorganic Nanoparticles :

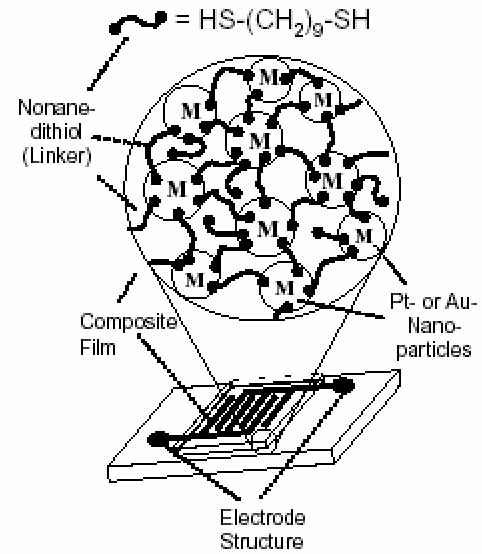
- Increasing the sensitivity of gas sensors by increasing surface area of the sensor increases.
- Miniaturizing the sensing devices

[Examples]

- ✓ SnO_2 (Tin oxide) nanoparticles detecting 3 ppm for CO_2, 15ppb for NO_2 and O_3, and 50 ppb for NO.
- ✓ WO_3 (Tungsten Oxide) based gas sensors to detect H_2S, N_2O and CO. 5 ppm of H_2S
- ✓ CNTs-FETs for CO, NH_3, NO_2, O_2, and H_2O sensor
- ✓ $ZnFe_2O_4$ (Zinc Ferrite) nanoparticles for VOC sensor
- ✓ ZnO nanoparticles for VOC
- ✓ Pd-Polyaniline nanocomposite for methanol sensor
- ✓ Au-decorated SnO2 nanobelt for CO sensor



Just detecting,
Not eliminating

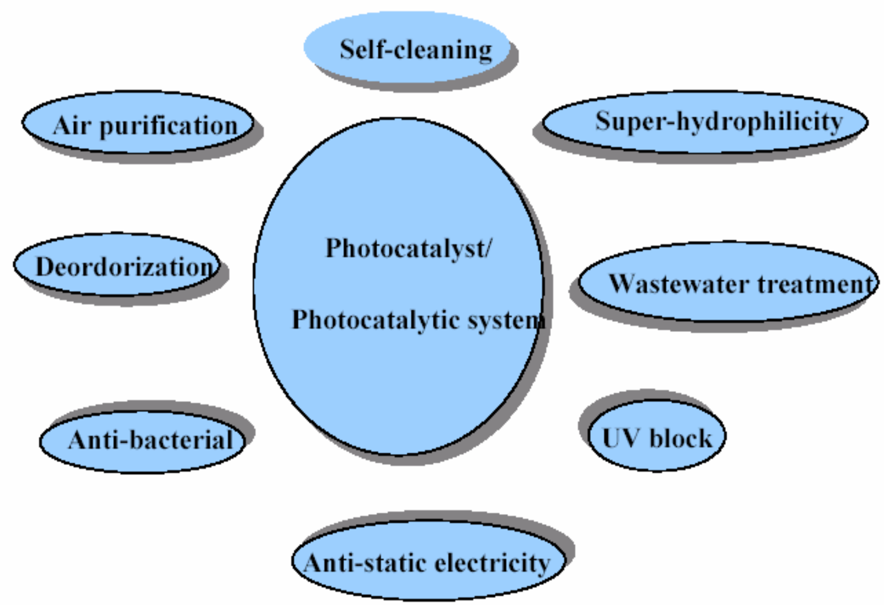


Applications of TiO_2 Photocatalyst

1. Japan
   - production of nano-size TiO_2 powder
   - sol containing TiO_2 photocatalyst for coating material
   - filter for air-cleaner
   - photocatalysis system

2. America and Canada
   - wastewater treatment

3. Europe
   - hybrid system of photocatalysis and other AOTs



NANO COMPOSITE PHOTOCATALYST

APPLICATIONS

HOUSE:
CEILING/WALL/FURNITURE/BLINDER/BED/SOFA/SEAT/PET THINGS, ETC

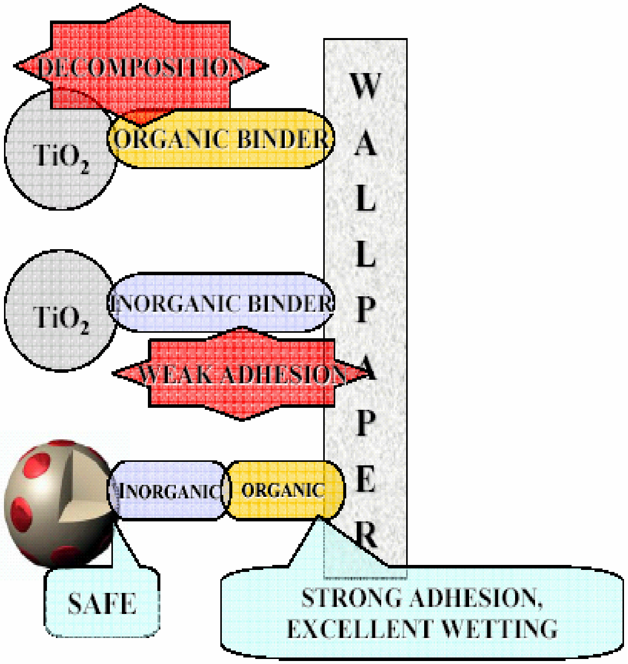
KITCHEN:
AGAINST FILTHY ODORS FORM COOKING & HOUSEHOLD GARBAGES

APPAREL:
VARIOUS CLOTHES / TEXTILES

FOOT WEAR:
INSOLE

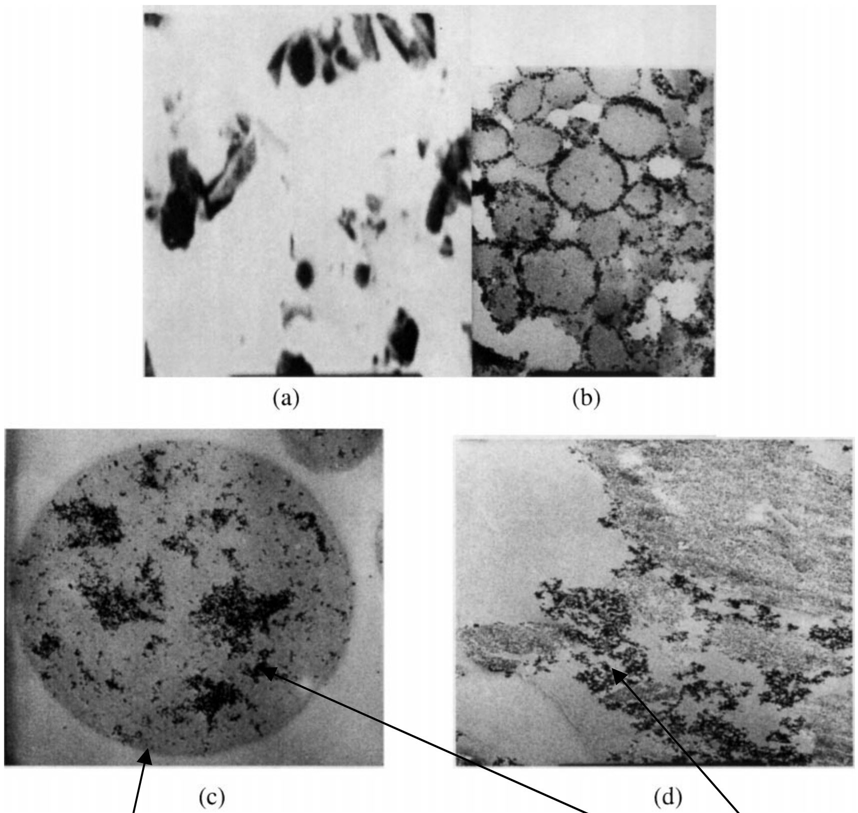
VEHICLE:
THE CEILING & AIR CONDITION VENT / FILTERS OF THE VEHICLE

OFFICE:
CEILING/WALL/SEAT/GARBAGES/AIRCONDITIONING VENT/FILTERS, ETC



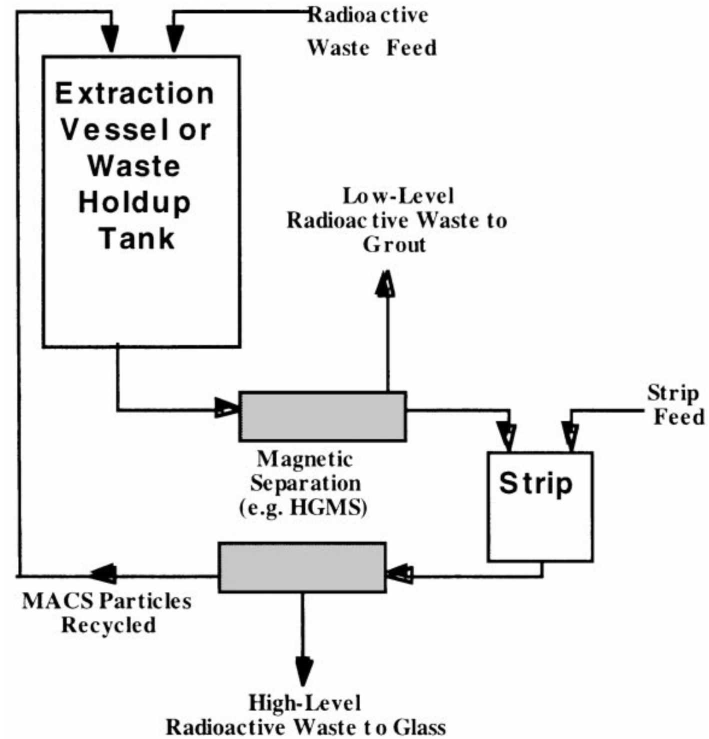
- ✓ **Only for air-purification**
- ✓ **It necessitates a binder and dispersant.**

Magnetic Nanoparticles embedded at Polymer Microparticles for Removal of Transuranic Pollutant



Micron-size Polymer particles

Magnetic Nanoparticles

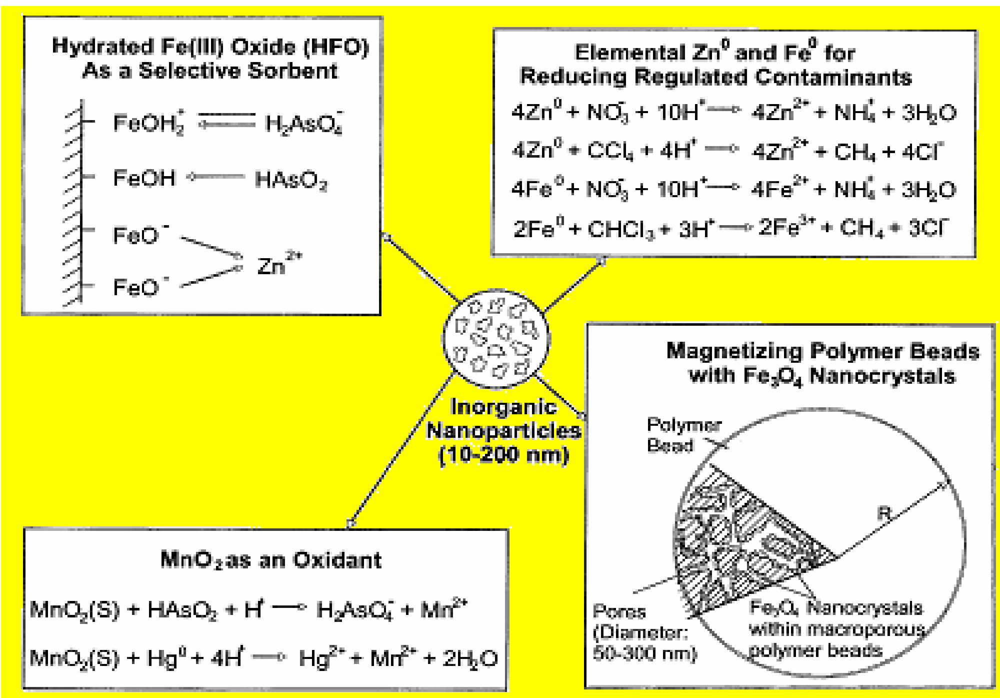


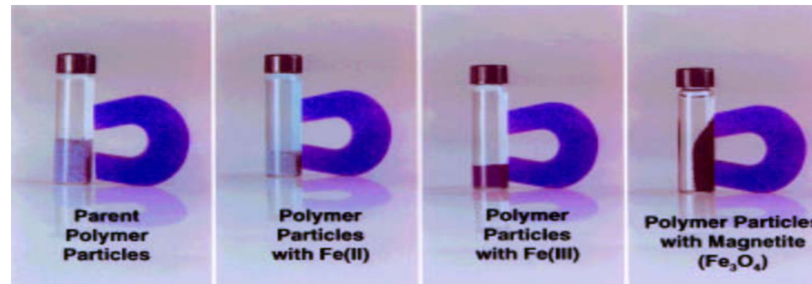
- **Hydrate Fe(III) oxides or Hydrated Fe(III) oxide nanoparticles embedded Polymer Microparticles**

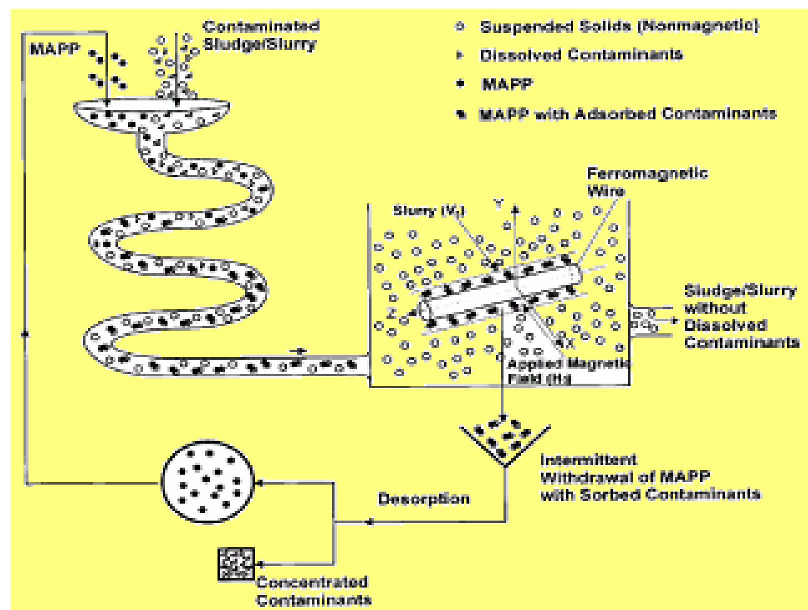
✓ **Selectively sorb dissolved heavy metal like zinc, copper or metalloids like arsenic oxyacids or oxyanions.**

✓ **Used only in batch or fixed column process.**

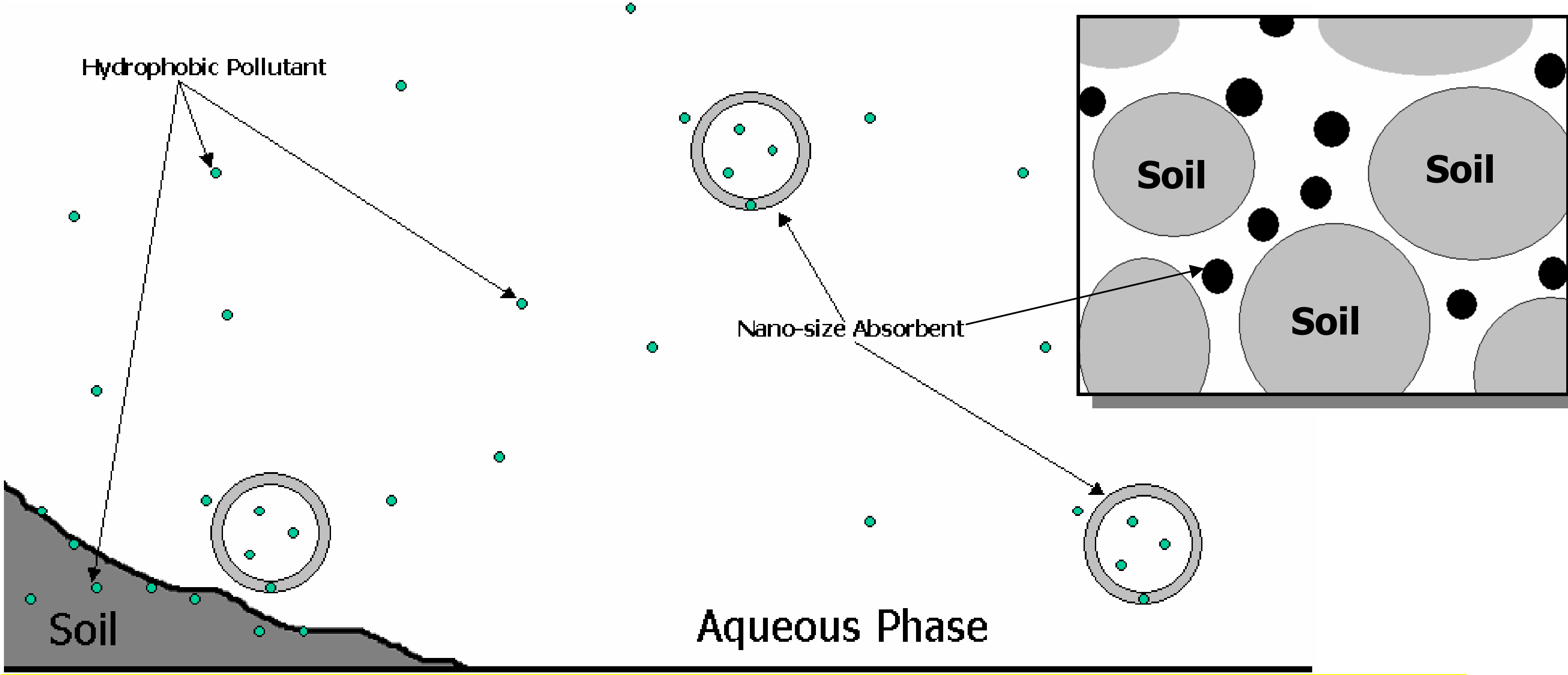
✓ ***In-situ washing or flow through process is not possible.***







Amphiphilic Organic Nanoparticles for In-situ Removal of Hydrophobic Pollutants From Soil and Water

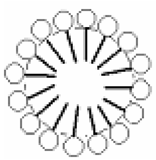


Nano-size Absorbent: Amphiphilic Nanoparticles

- ✓ Interfacial activity
- ✓ Solubilizing hydrophobic pollutants
- ✓ Dispersion stability at aqueous phase
- ✓ Freely flowing through soil pores (much smaller than soil pores)
- ✓ Easy recovery

Amphiphilic Nanoparticles

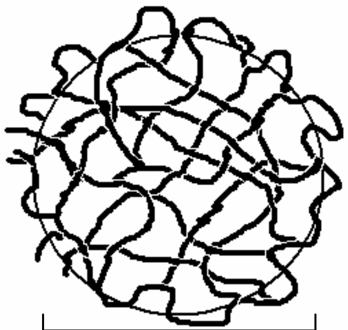
Surfactant micelle



1 – 5 nm

- ✓ Cheaper than ABC
- ✓ a **few nm size**
- ✓ **easily breakable**
- ✓ **hard to separate**
- ✓ **strong adsorption**

ABC nanoparticle
(Amphiphilic Block Copolymer)



20 – 100 nm

- ✓ **too expensive ($100 – 2,000 / Kg)**
- ✓ **very complicated synthetic process**
- ✓ **hard to control hydrophilicity or hydrophobicity**
- ✓ **easily breakable**
- ✓ **Not high molecular weight**

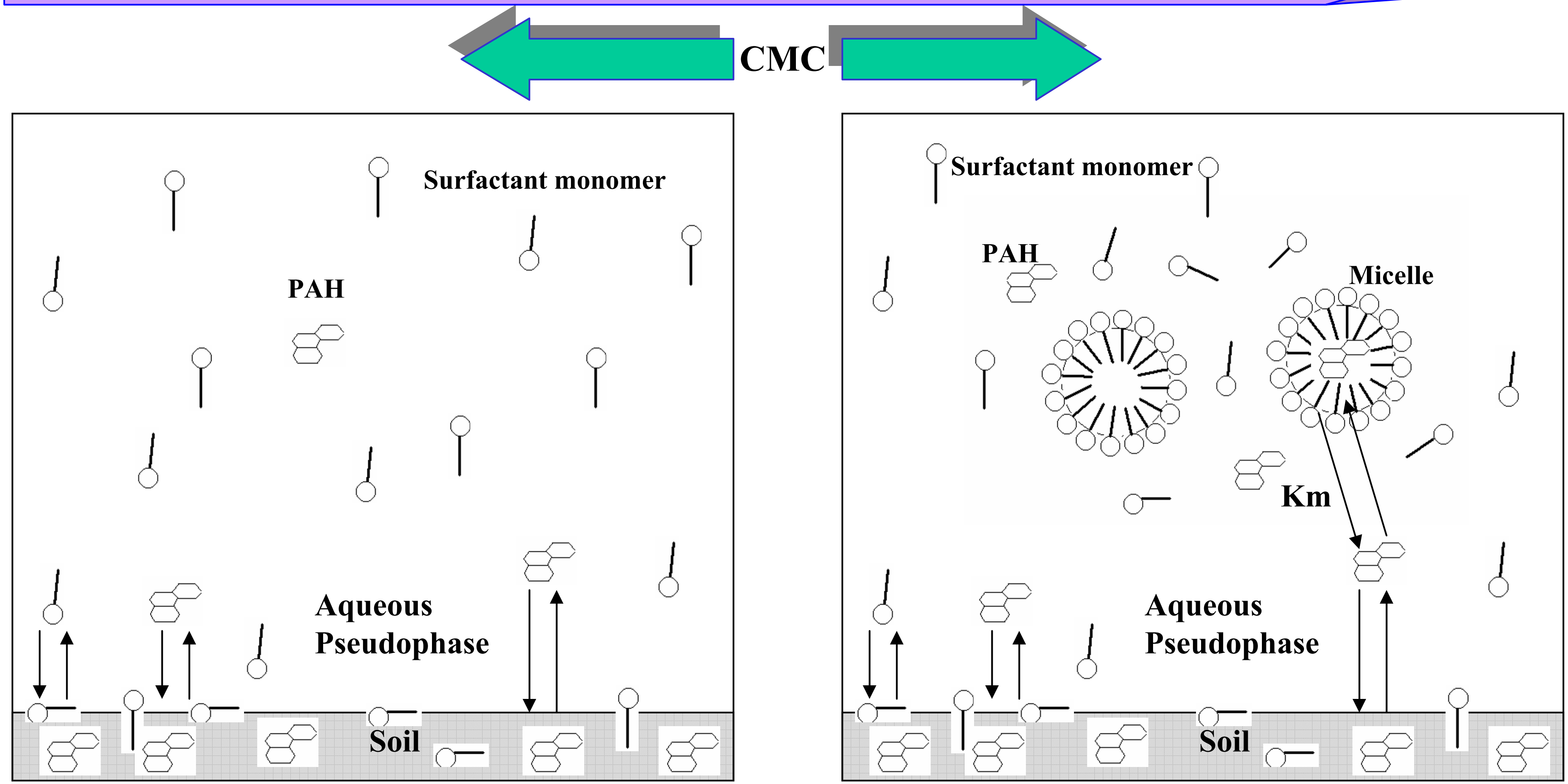
Ex) Polystyrene-b-Polyethylene oxide
Polystyrene-b-PVP
NORCOOH(2-norbornene-5,6-dicarboxylic acid)
$(MTM)_{500}(NORCOOH)_{50}$ block copolymer

Improving efficiency of conventional environmental Process

- ✓ Surfactant-enhanced Desorption Process
- ✓ Micellar-enhanced Ultrafiltration
- ✓ In-situ Surfactant-enhanced Soil Washing Process

- ✓ High and strong sorption onto a soil
- ✓ Easily breakdown (secondary contamination)
- ✓ Very difficult to be separated and recovered
- ✓ Blocked soil pores by newly formed oil emulsion

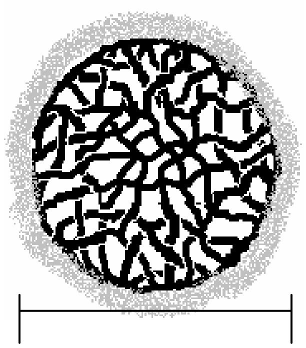
Schematic Presentation of Aqueous Pseudophase containing Surfactant



- ✓ At lower or equal to CMC, surfactant can not extract a pollutant because of large amount adsorption of surfactants onto soil.
- ✓ At higher than CMC, large amount of surfactant are also adsorbed because surfactant micelles are easily break down.
- ✓ Adsorption of surfactant act as an additional soil contaminants and necessitate additional washing process.

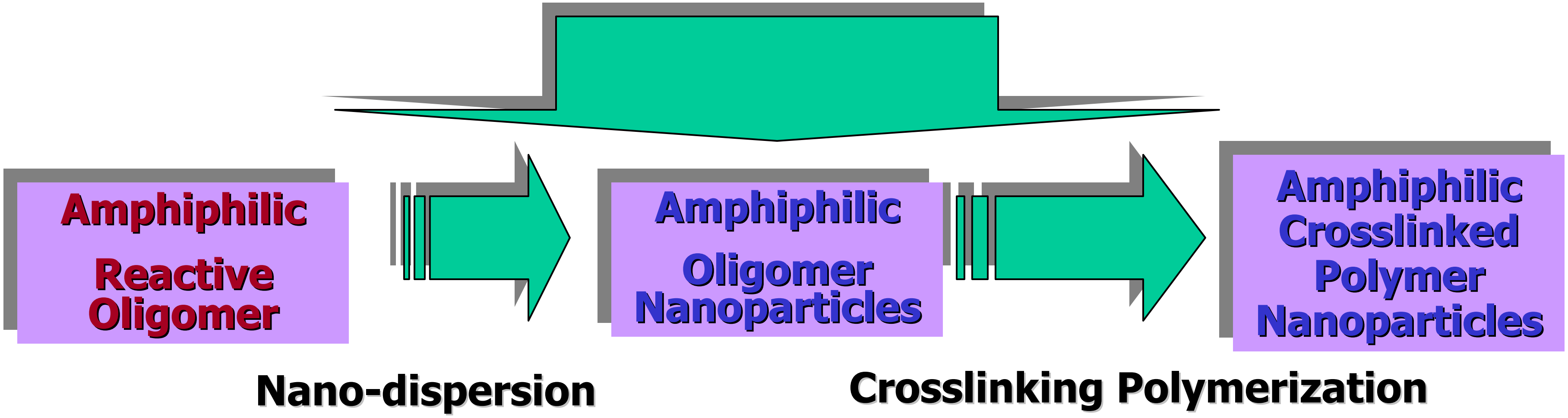
- ✓ **Cheaper than Amphiphilic Block Copolymer**
- ✓ **Easier process that the synthesis of Amphiphilic Block Copolymer**
- ✓ **Lower degree of sorption onto a soil than Surfactant**
- ✓ **Much lower CMC than surfactant**
- ✓ **Bigger than Surfactant micelles**

A New Type of Polymer Nanoparticle



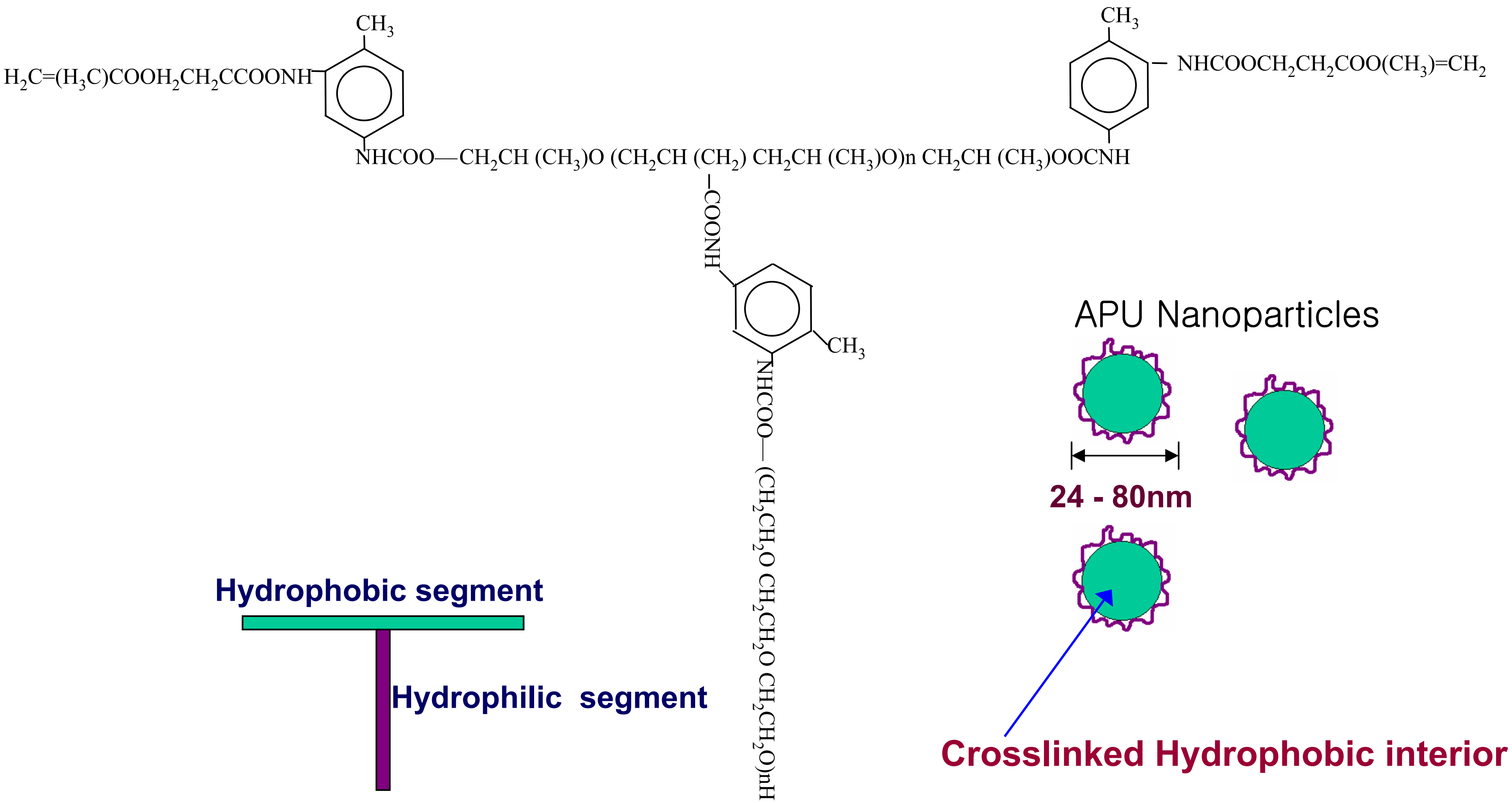
20 – 100 nm

Amphiphilic Polymer Nanoparticles Synthesized Using Amphiphilic Reactive Oligomer



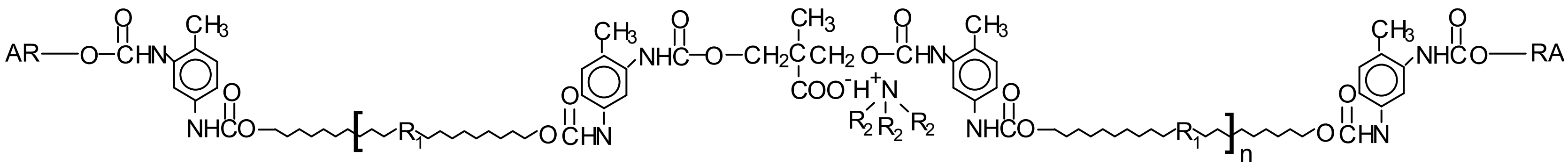
- ✓ Cheaper than amphiphilic block copolymer
- ✓ Simpler and easier process than the synthetic process of amphiphilic block copolymer
- ✓ Easy to vary length and ratio of hydrophilic/hydrophobic segments
- ✓ 20 -100 nm size (Bigger than surfactant micelle)
- ✓ Lower degree of sorption onto a soil
- ✓ Very strong nano-structure owing to chemical cross-linking
- ✓ extremely low cmc and adsorption

Amphiphilic Reactive Oligomer: Urethane Acrylate Nonionomer (UAN)

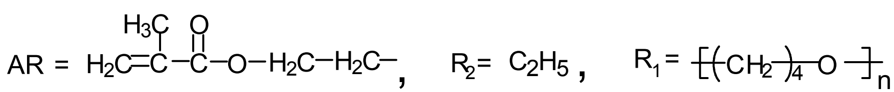


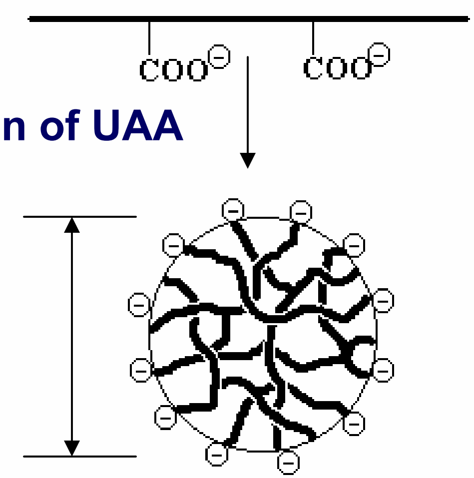
Mw = 3450 - 7600

Amphiphilic Reactive Oligomer: Urethane Acrylate Anionomer (UAA)



Mw = 2350 - 8400

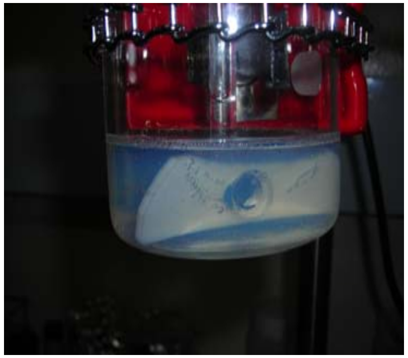




Soap-free emulsification of UAA

Average particle size: 40 -85nm

Preparation of Amphiphilic Polymer Nanoparticles



UAN or UAA

Amphiphilic Oligomer

Mixing with water

Amphiphilic Oligomer Nanoparticles

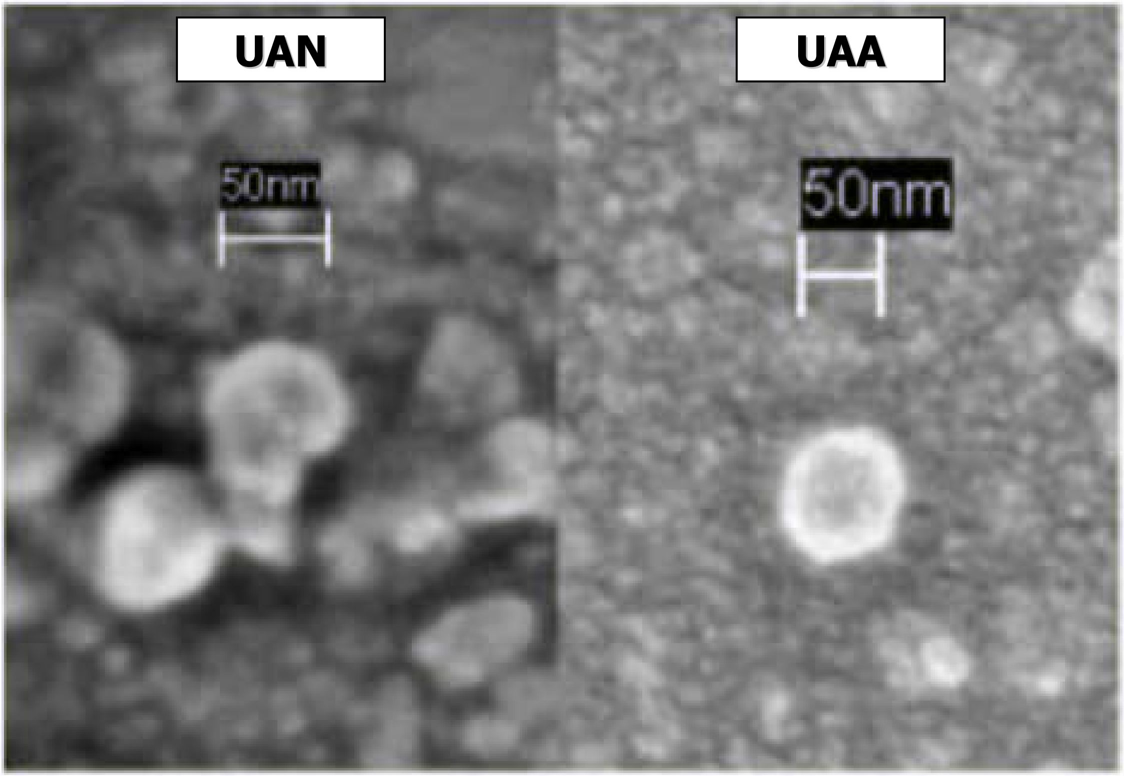
Crosslinking polymerization

ACPU or APU Polymer Nanoparticles

Amphiphilic Crosslinked Polymer Nanoparticles

Concentration : APU or ACPU nanoparticles in water phase (10 mg – 100,000mg/L)

FE-SEM image of UAA and UAN nanoparticles dispersed at aqueous phase



W. Tungittiplakorn, et al., Environ. Sci. & Technol. 2004, 38, 1605
(Dept. of Civil & Environmental Engineering, Cornell University)

Soil Washing Efficiency

Amphiphilic Polymeric Nanoparticles vs. Surfactants

Surfactants

•Nonionic Surfactant : Triton X-100 (TX-100) (CMC = 110mg/L, HLB = 13.5)
TWIN 80 (CMC = 15.7 mg/L, HLB = 15.0)
Brij 30 (CMC = 20 mg/L, HLB = 9.7)

• Anionic Surfactant : SDS (CMC = 2100 mg/L)

Amphiphilic Polymeric Nanoparticles

• Amphiphilic Polyurethane Nanoparticles
: Anionic Polyurethane (ACPU) Nanoparticles
Nonionic Polyurethane (APU) Nanoparticles

Model Medium

- ✓ Soil : Aquifer soil obtained from Newfield, NY

  Organic carbon content = 0.049± 0.012%

  47.2% of sand = 0.1-0.25mm

  47.6% of sand = 0.25-0.5mm

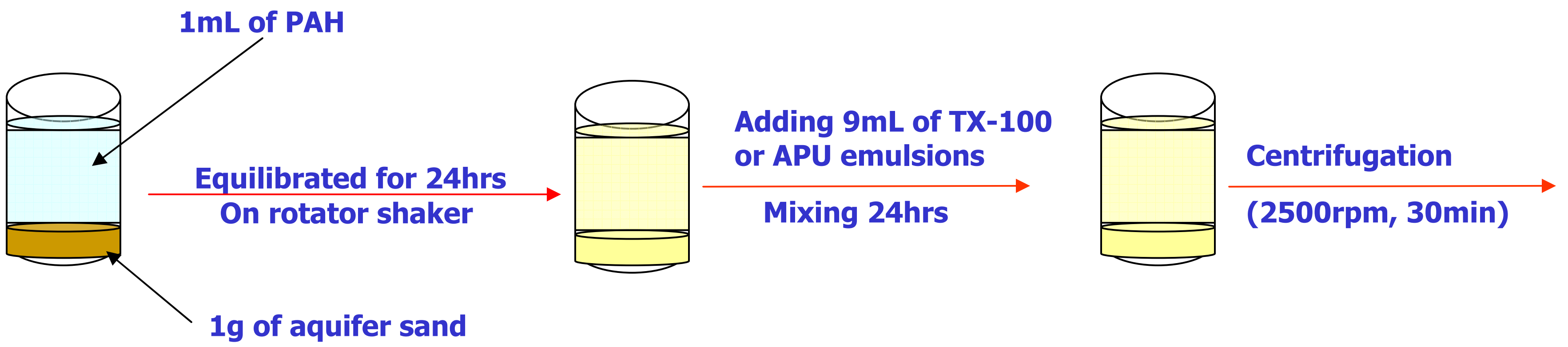
Model Pollutant

- ✓ Model pollutant : phenanthrene (PAH)

  (9-14C, 13.1μCi/mol, Sigma Chemical Co)

- ✓ Liquid Scintillation Counter: LS 6800 (Beckmann)

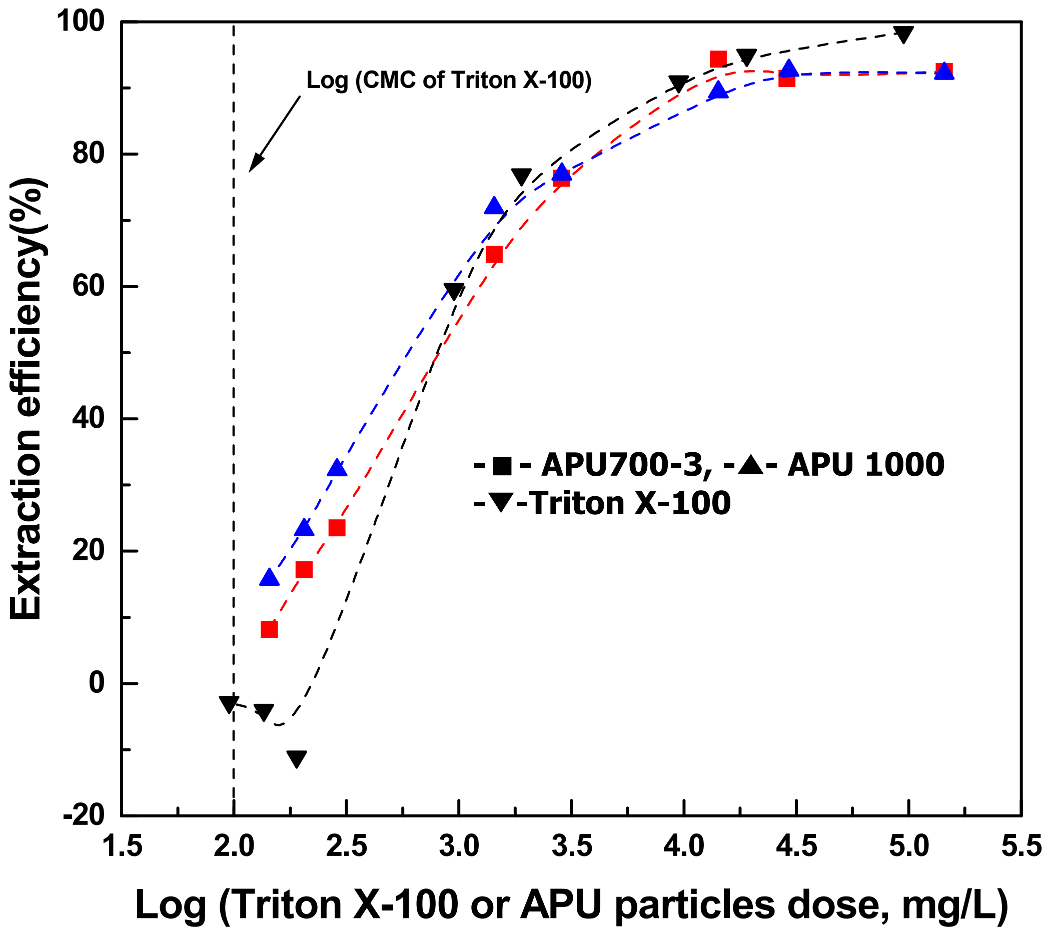
Batch Experiments Procedure for Determining Desorption of Sorbed PAH in the Presence of Surfactants or APU (ACPU) Nanoparticles



1. $K_d = [HOC]_s/([HOC]_w + [HOC]_{mic})$
   = (mol of HOC sorbed/g of solid)/(mol of HOC in aqueous and micellar solution/L)

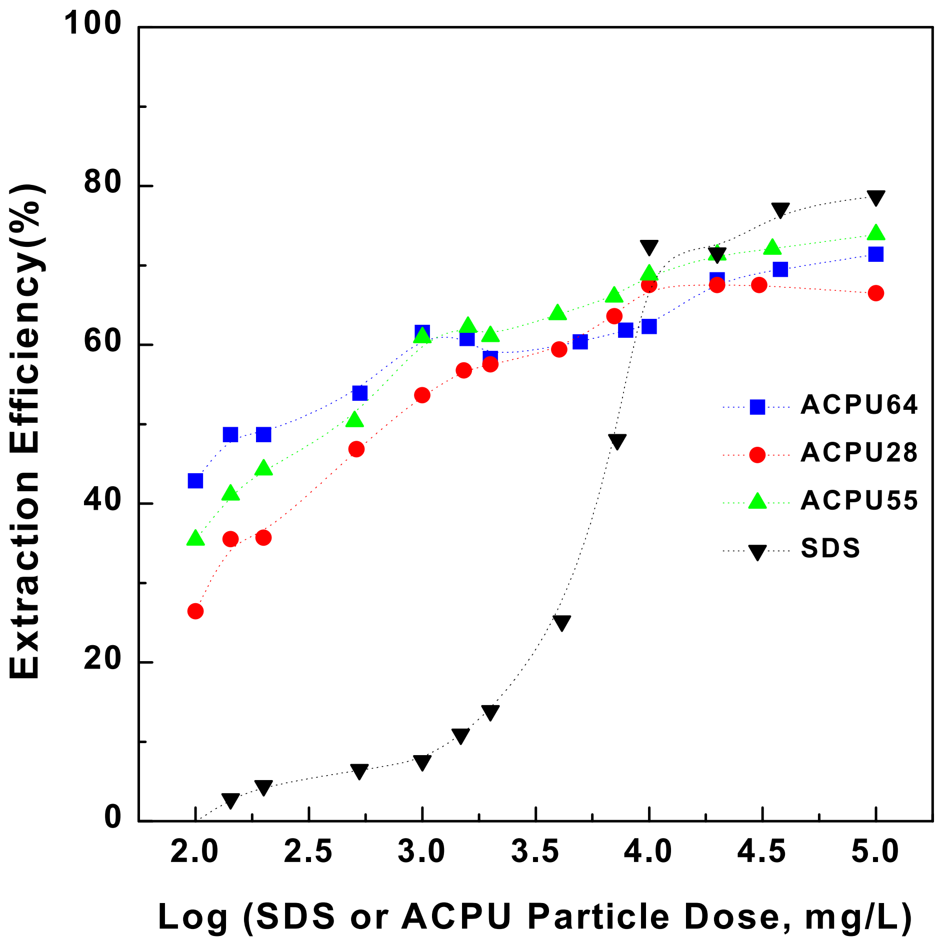
2. Extraction efficiency = (desorbed amount of phenanthrene)/(sorbed amount of phenanthrene on aquifer sand) X 100 (%).

Extraction efficiency of APU particles and Triton X-100 solution

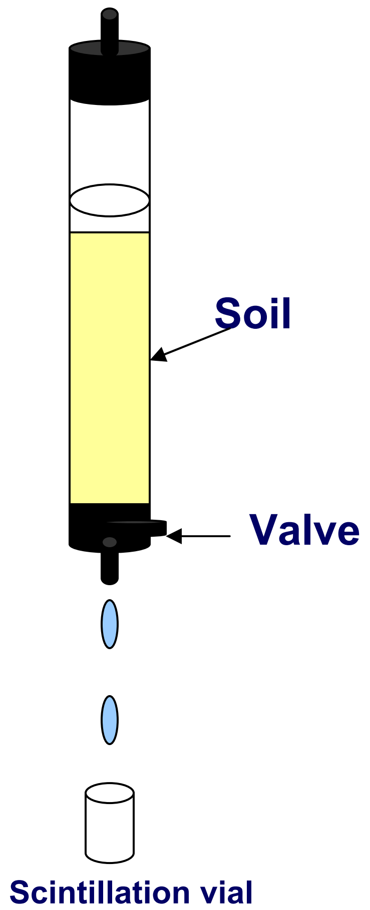


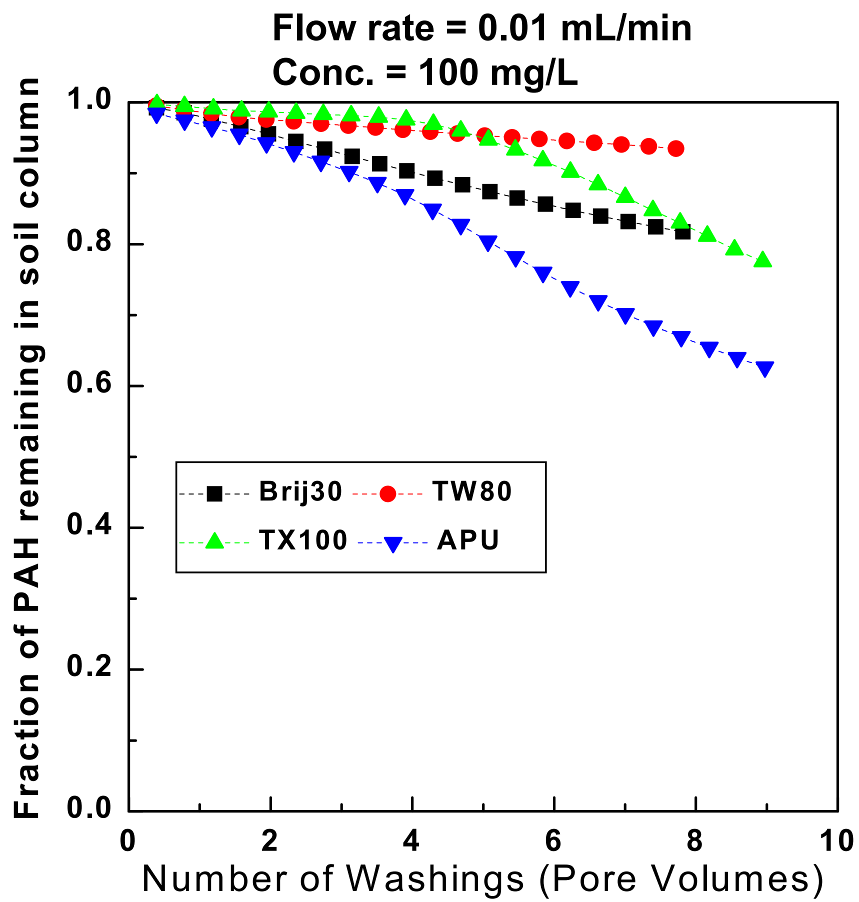
Extraction efficiency = (desorbed amount of phenanthrene)/(sorbed amount of phenanthrene on aquifer sand) X 100 (%).

Extraction efficiency of ACPU particles and SDS solutions

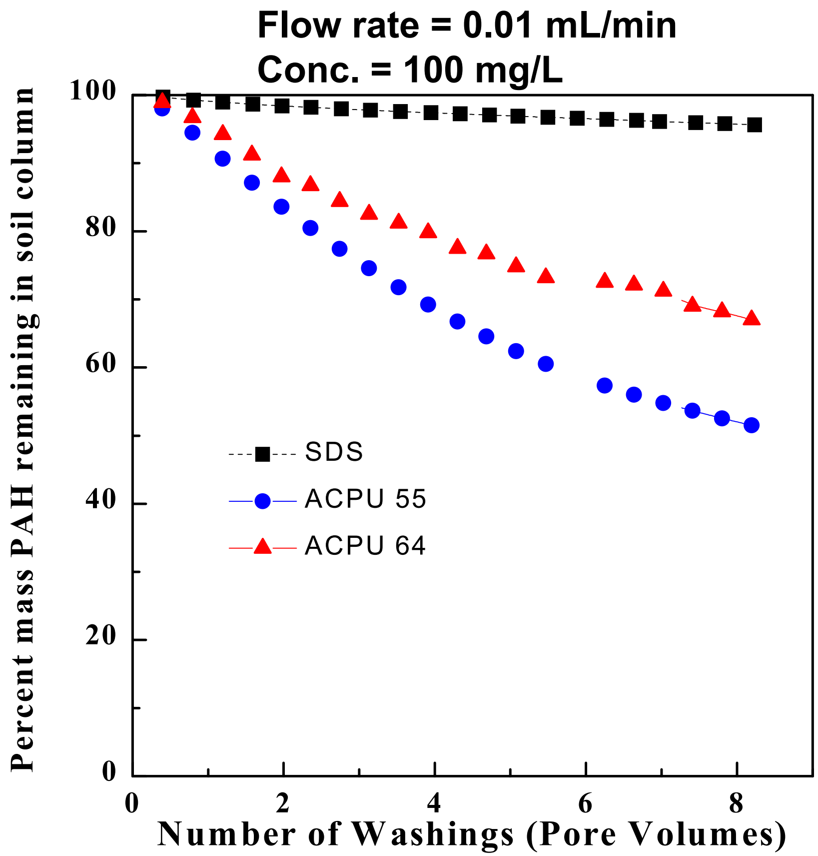


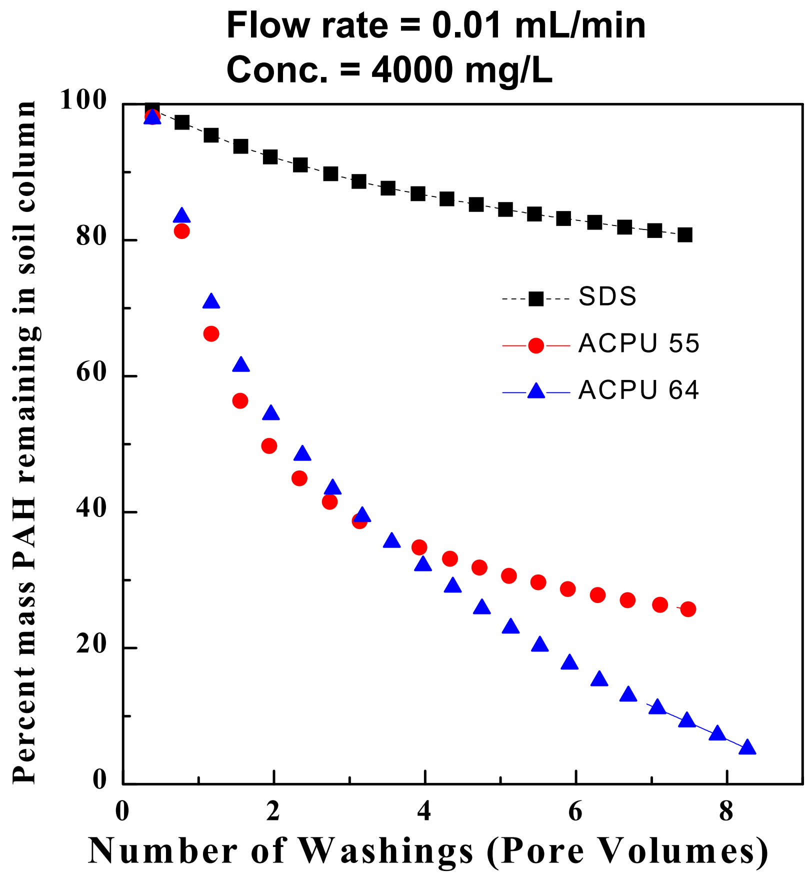
In-situ extraction of sorbed phenanthrene from soil using ACPU (APU) nanoparticles and surfactants



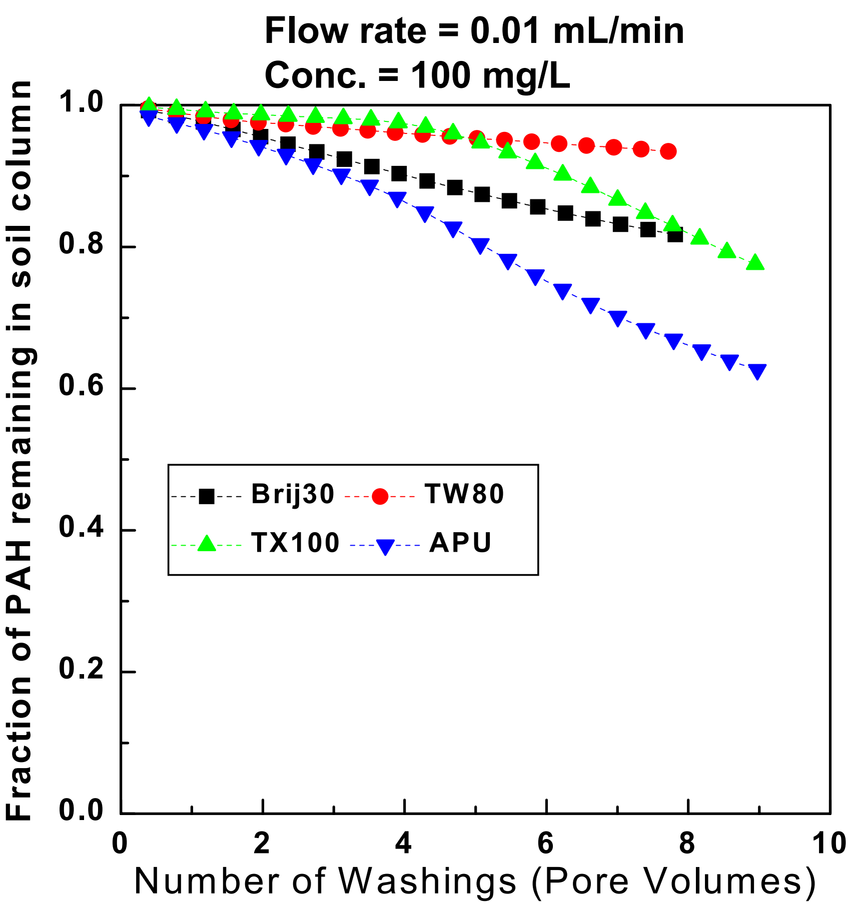


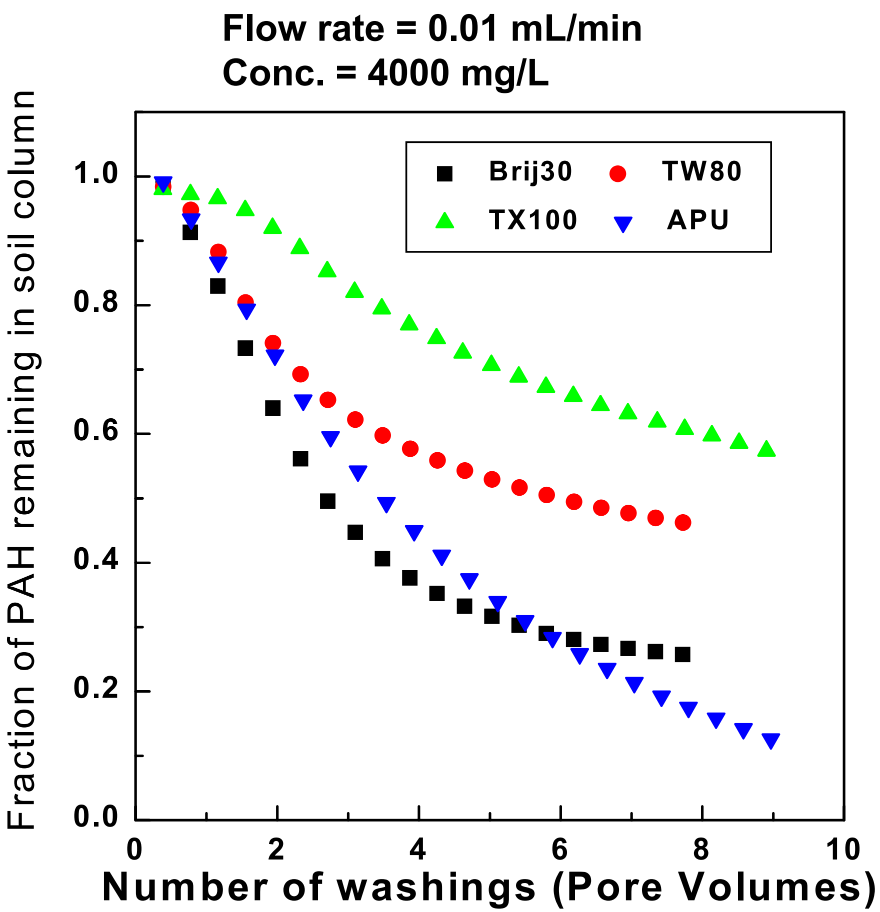
In-situ extraction of sorbed phenanthrene from soil Using ACPU nanoparticles and SDS solutions





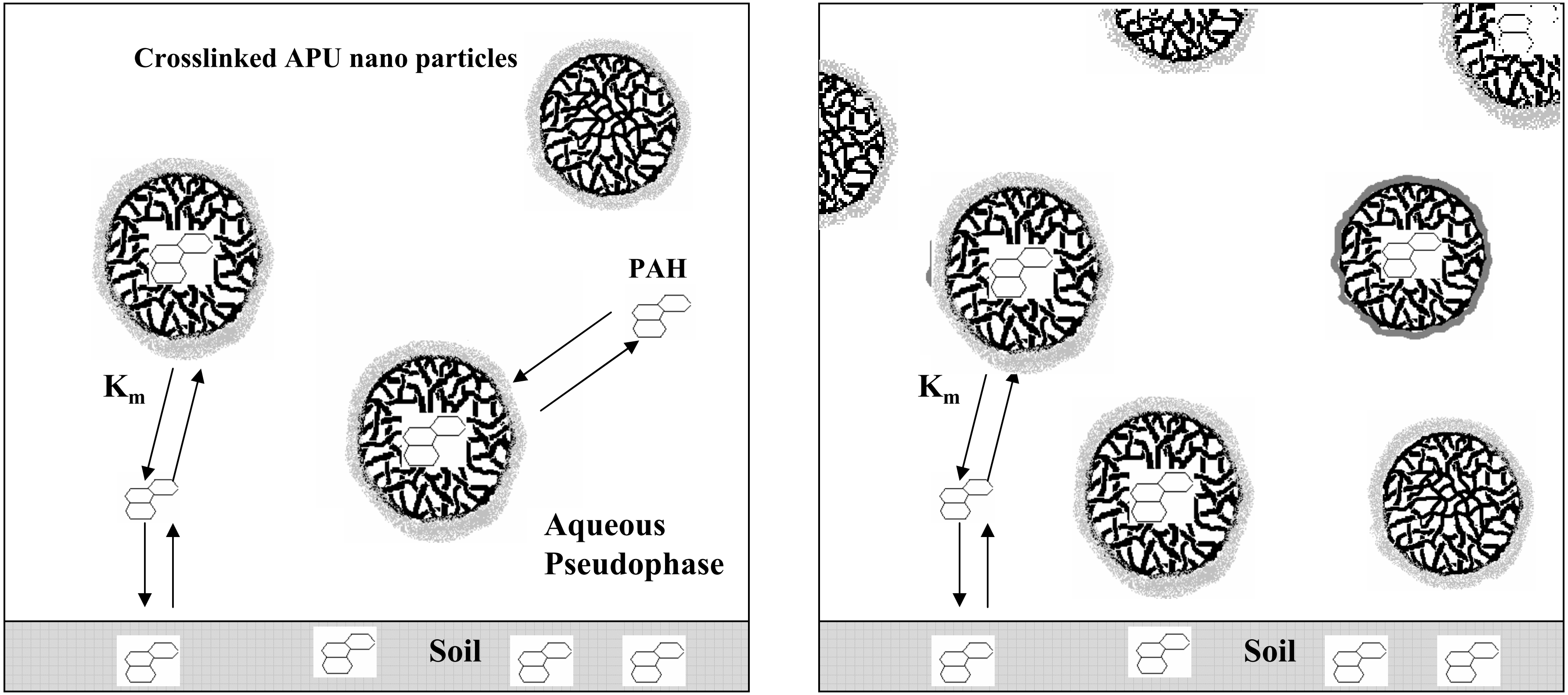
In-situ extraction of sorbed phenanthrene from soil Using APU nanoparticles and nonionic surfactants





Schematic Presentation of Aqueous Pseudophase Containing Polymeric Nanoparticles

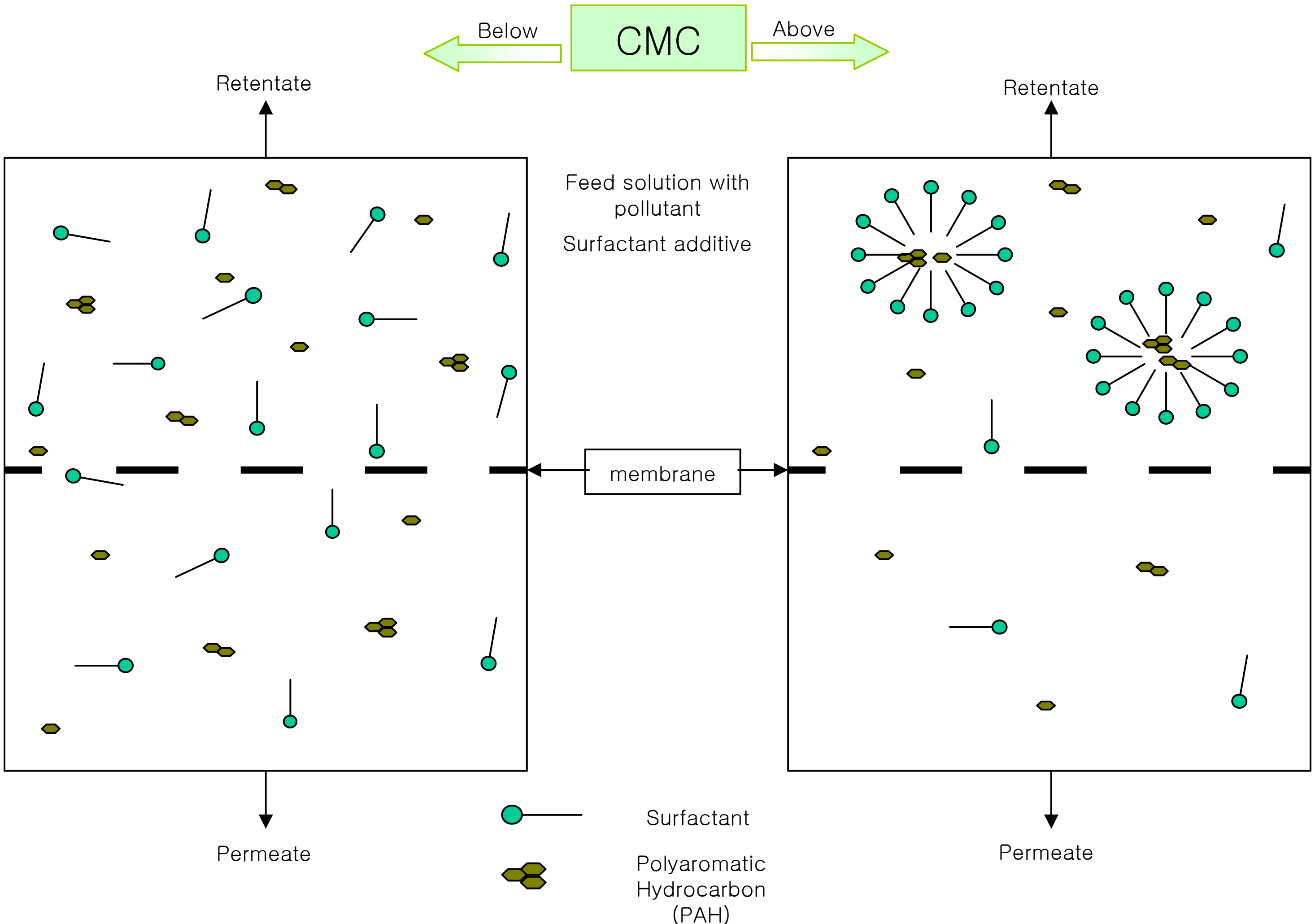
CMC is extremely low !!



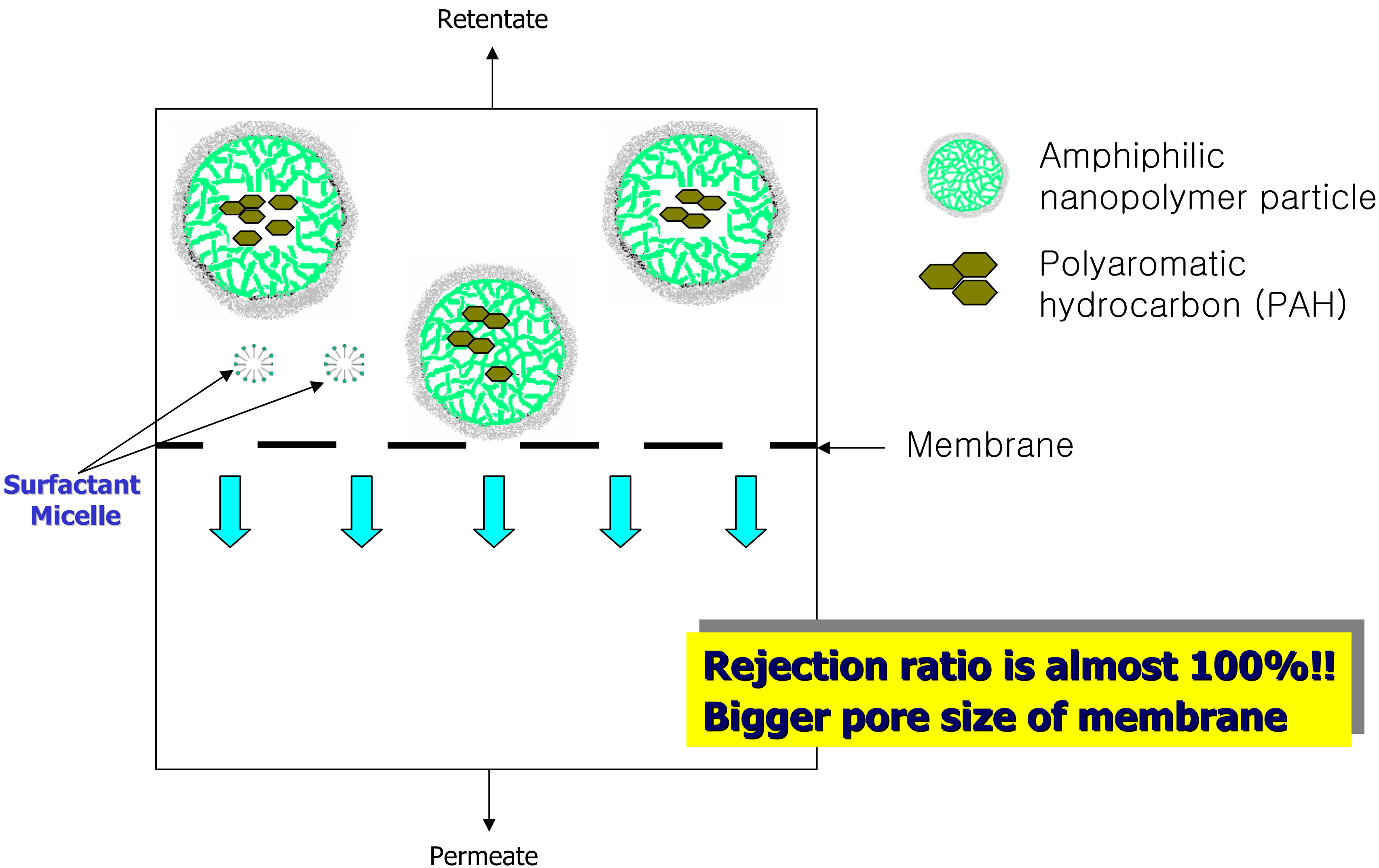
✓ **Polymeric nanoparticles can extract a pollutant at very low concentration because their extremely low CMC.**
✓ **Adsorption onto soil are very low because of chemically crosslinked strucutre.**

MEUF (Micelle-enhanced ultrafiltration)

- Very low water solubility but extremely harmful for human
- With very small amounts, tremendous volume of water are contaminated
- MEUF is one of the most effective process for separating hydrophobic pollutants (Better than incineration, oxidation, supercritical oxidation process)

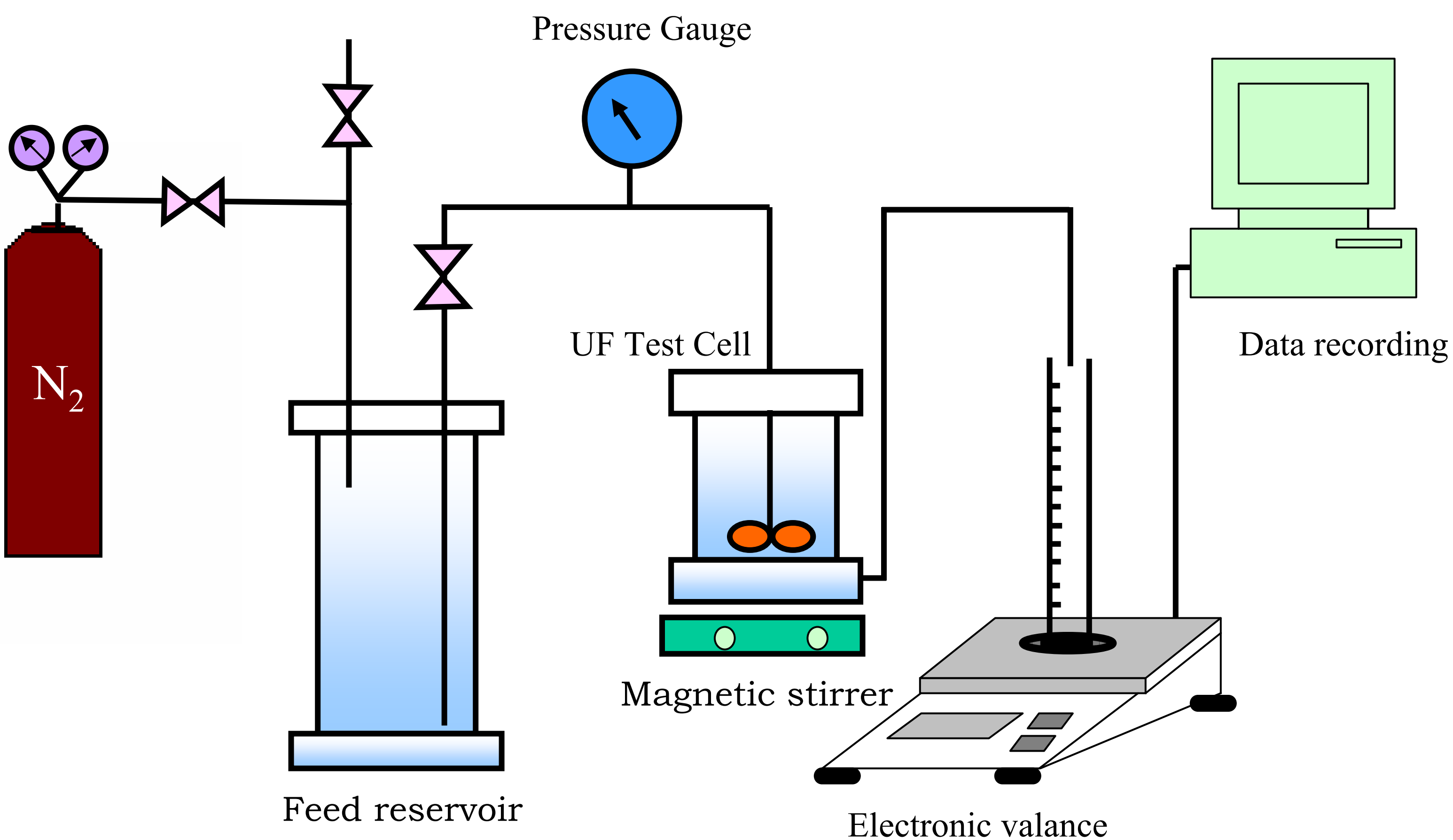


NEUF (Nanoparticle-enhanced ultrafiltration)



Rejection ratio is almost 100%!!
Bigger pore size of membrane

Dead-end stirred cell filtration system



Rejection rates of ACNP and SLS solutions

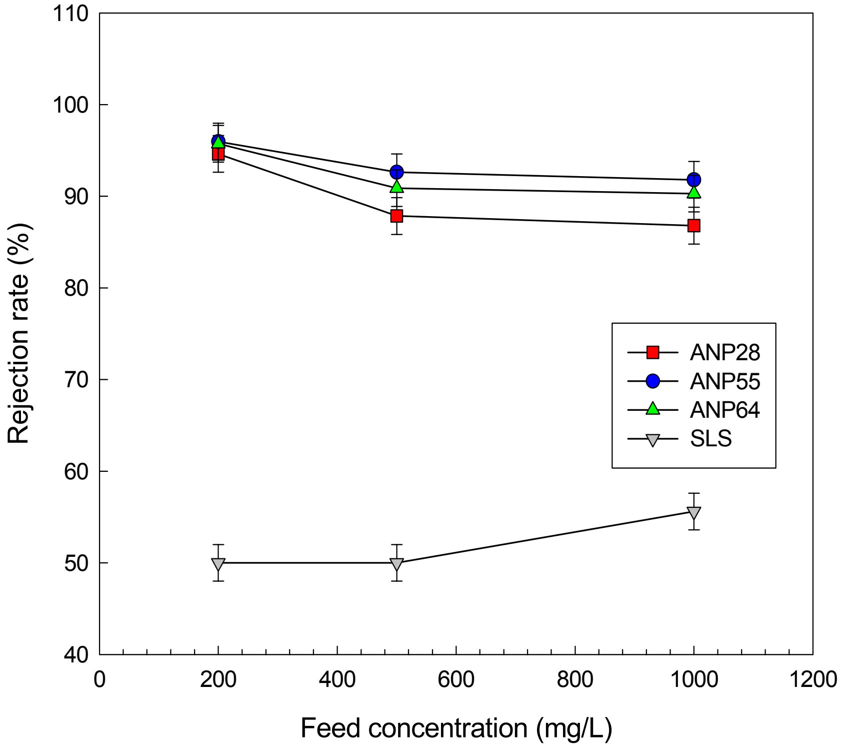


Fig. 7.The variation of rejection rate of ANP particles and SLS surfactants with concentration at 2 kgf/㎠.

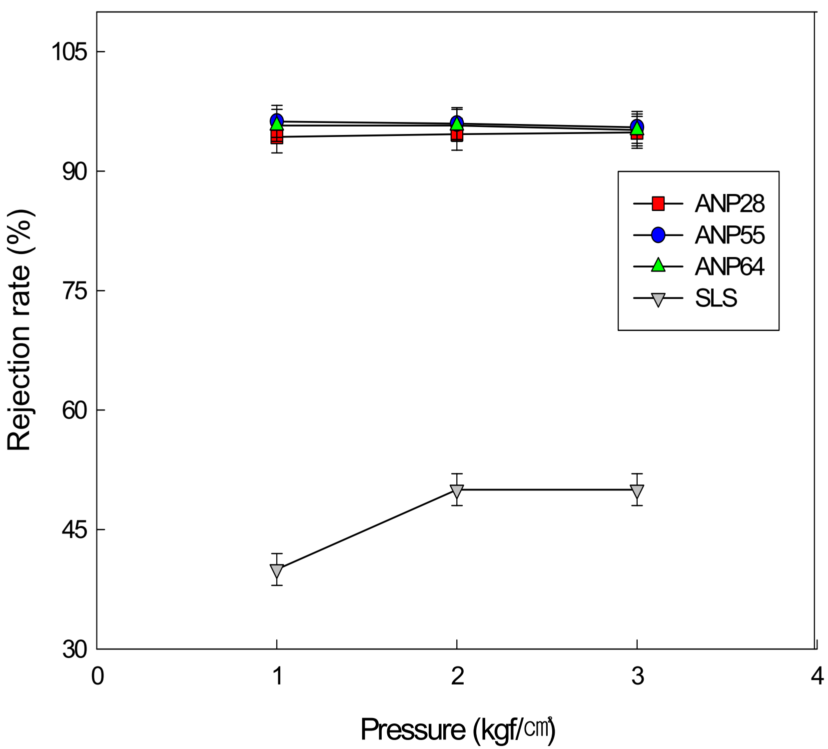


Fig. 8. The variation of rejection rate of ANP particles and SLS surfactants at different transmembrane pressure, where the concentration of solutions is 200 mg/L.

❑ **In-situ amphiphilic Polymer Nanoparticle-enhanced Soil Washing process**
(In-situ APN-enhanced Soil Washing Process)

❑ **Amphiphilic Polymer Nanoparticle-enhanced Ultrafiltration process**
(ANP-UF Process)

Fusion Technology of NT and ET

New environmental process can be created

by Amphiphilic Polymer Nanoparticles

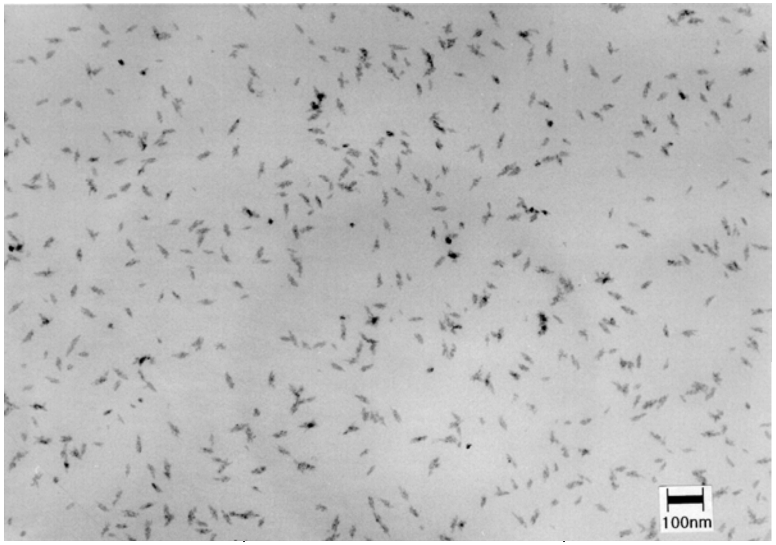
Amphiphilic Reactive Oligomers
(UAN and UAA)

Another Applications of Amphiphilic Reactive Oligomer

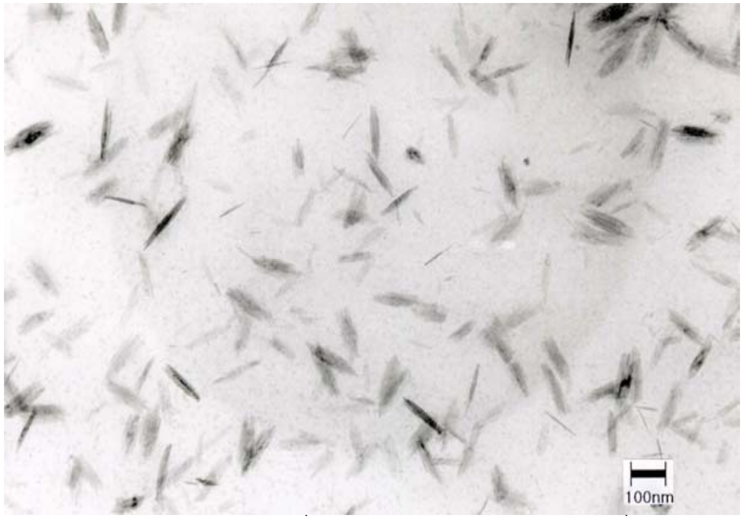
- ✓ Synthesis of Nanoparticles with much cheaper price
- ✓ Simple Process
- ✓ Easy to Control of Particle Size
- ✓ Easy to Make Thin Nanocomposite Film

- ❑ Synthesis of Magnetic Nanoparticles Dispersed Polymer Films
- ❑ Synthesis of CdS and Ag Nanoparticles Dispersed Polymer Films
- ❑ Synthesis of CdS and Ag Nanoparticles Dispersed at Water and Toluene
- ❑ Nano-dispersant for Silica and Clay Nanoparticles
- ❑ Dispersant for Graphite and Carbon Nano Tube (CNT)

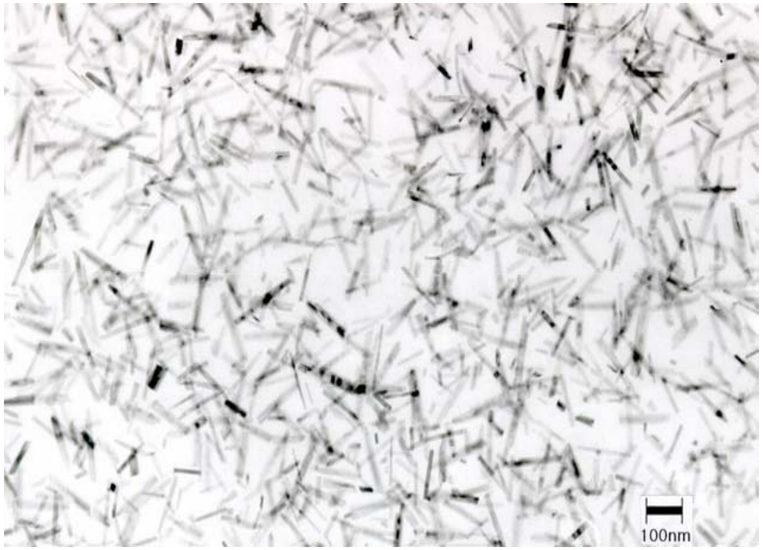
TEM Images of Magnetic Nanoparticles Dispersed in PU Films



UAN NO-Solvent

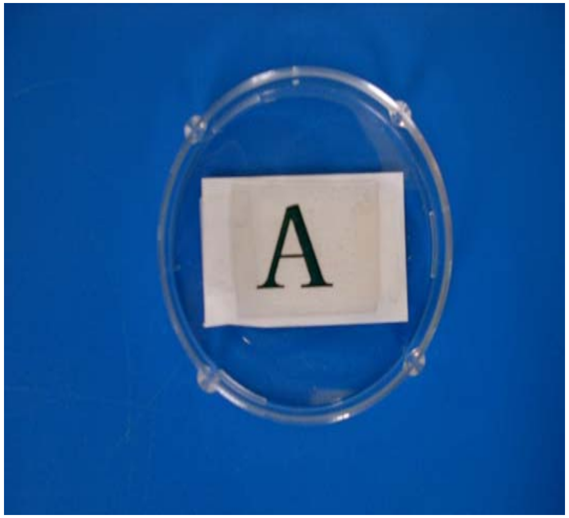


UANH gel

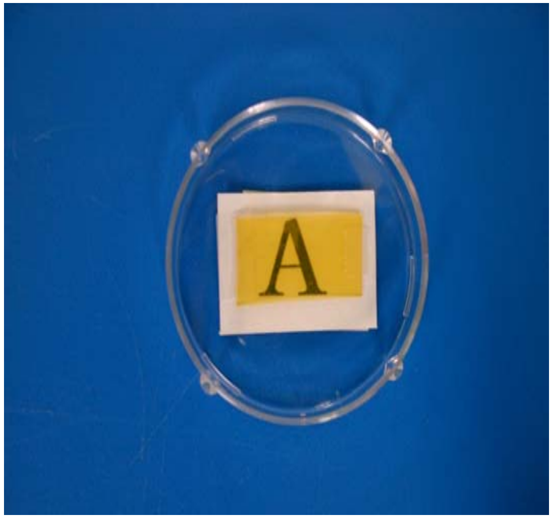


UAND gel

Appearance of PU Films Containing CdS Nanoparticles



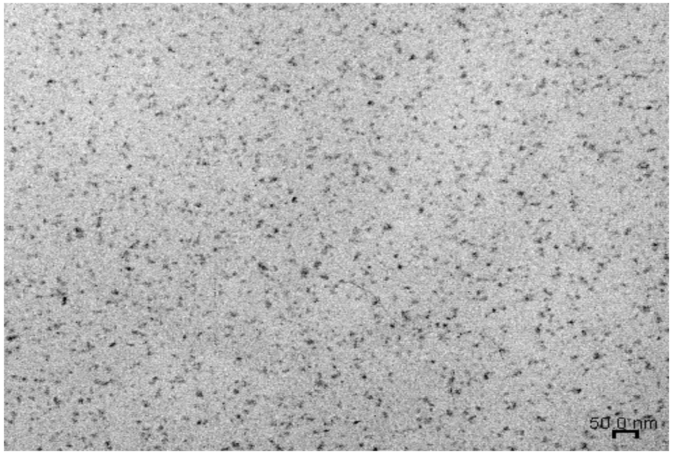
Neat UV-cured PU film

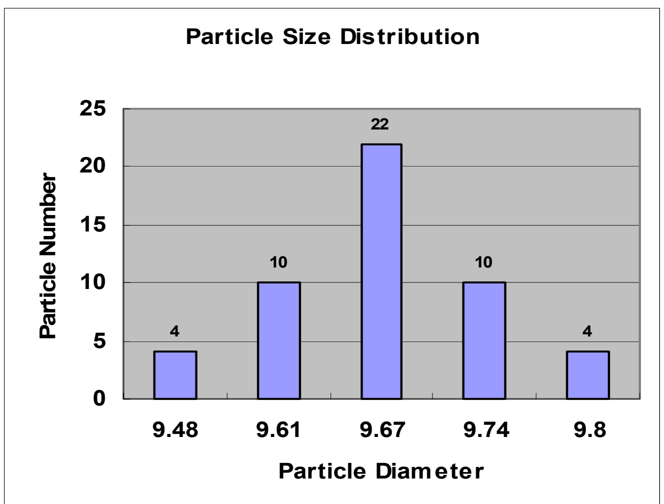


PU film containing CdS nanoparticles

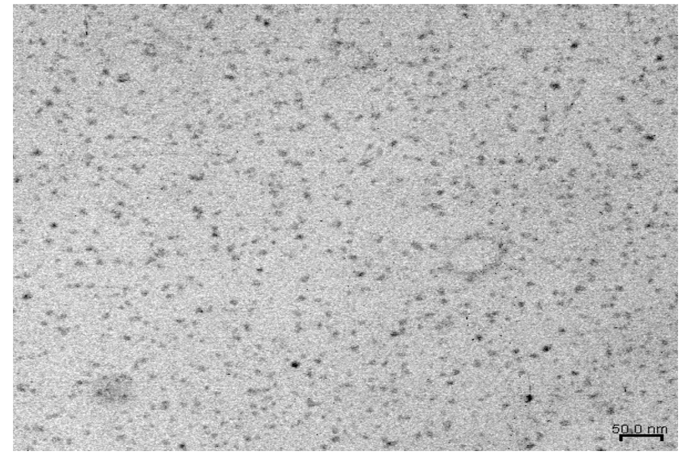
TEM of Semiconductor nanoparticles dispersed in PU films

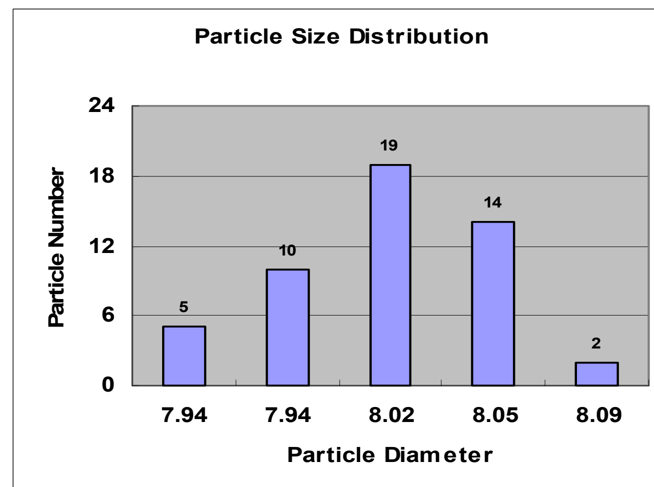
◈ **PMUA 700-3(3g) + Cd (1%) +THF(1.5g)**
Average Particle Diameter : 9.67nm





◈ **PMUA 700-3(3g) + Cd (1%) +Methanol(1.5g)**
Average Particle Diameter : 8.02nm

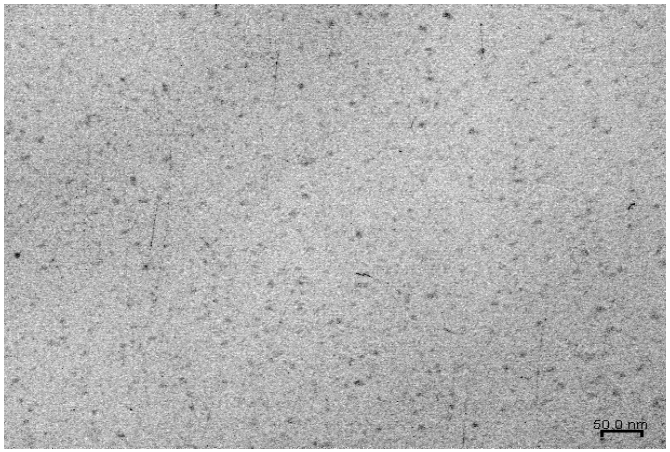


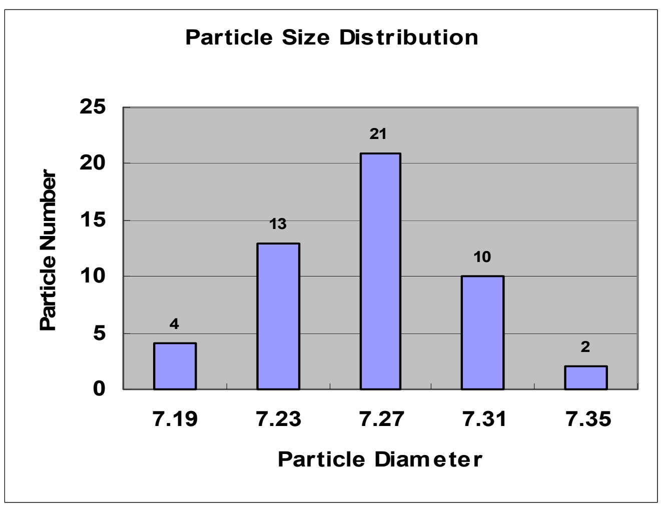


TEM of Semiconductor nanoparticles dispersed in PU films

◈ PMUA 700-3(3g) + Cd (1%) +DMAc(1.5g)

Average Particle Diameter : 7.26nm





✓ CdS was successfully reduced by sodium sulfide in a hydrophilic nanodomain.

✓ it shows the formation of a stable aggregation nucleus without agglomerization among the hydrophilic nanodomains.

✓ CdS nanoparticles were successfully dispersed in polyurethane film and obtained a narrow particle size distribution

✓Solvents of low dielectric constant formed a great nanoparticles due to forming larger hydrophilic doma

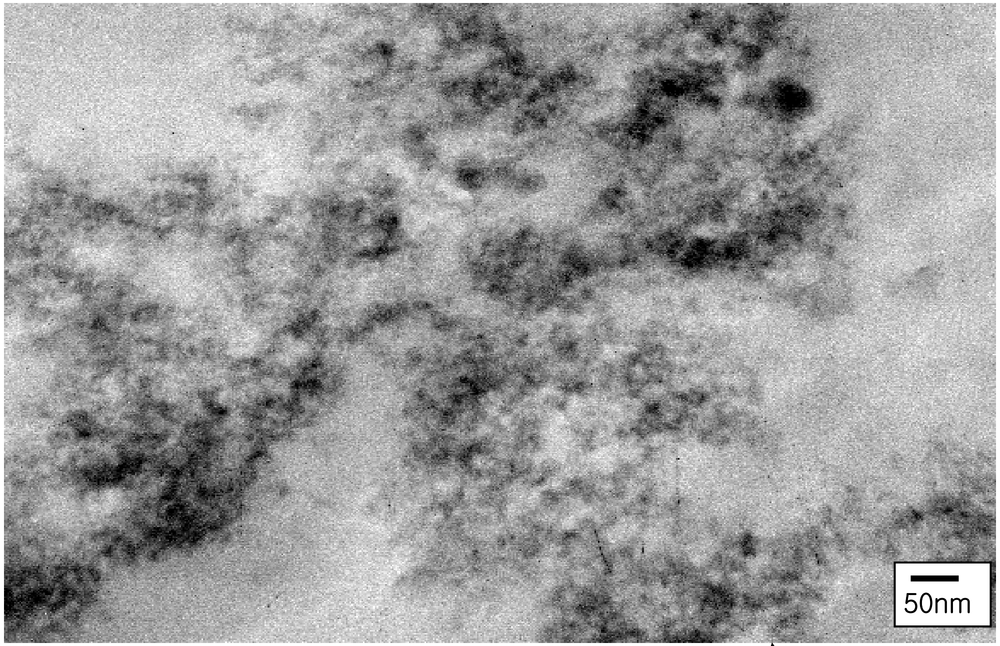
- Toluene dielectric constant: 2.38
- THF dielectric constant: 7.6
- Methanol dielectric constant: 32.6
- DMAc dielectric constant : 37.8

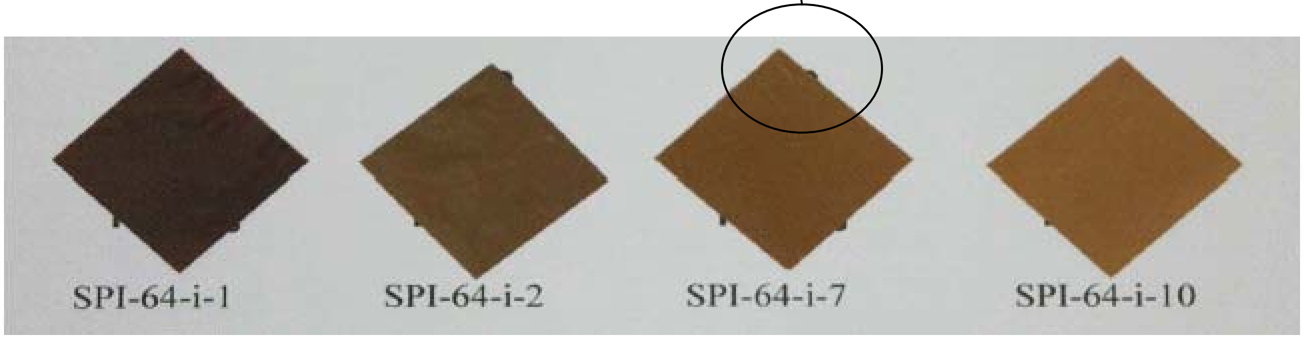
Nano-Silica Powder and Silica Nanoparticles Dispersed in a solvent

Nano-Silica Powder

Silica Nanoparticles dispersed in a solvent

TEM image of Sulfonated Polyimide Containing Silica Nanoparticles





PEM membranes containing silica nanoparticles dispersed by aid of UAN

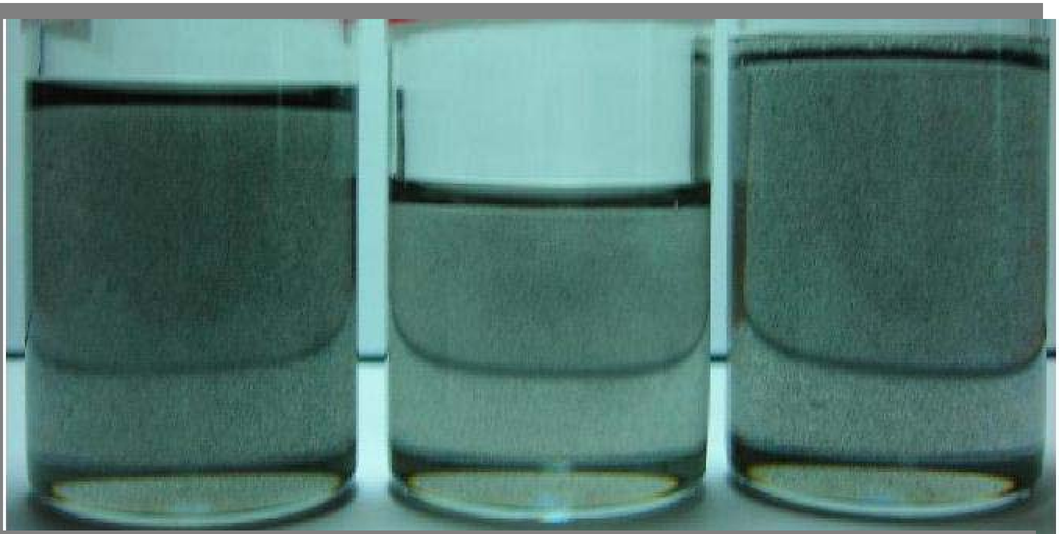
- ✓ **Improved chemical stability**
- ✓ **Hydrolytic stability**
- ✓ **Reduced methanol permeability**
- ✓ **Not sacrificing conductivity**

√ Introduction of UAN containing urethane groups: enhancement in elongation

Samples	Compatibilizer	Solvent	Silica content (wt %)	Tensile strength (Mpa)	Elongation (%)	Hydrolytic stability (hr, 80 °C)[a]	Proton conductivity (10^{-2} S/cm)	
							Before	After
SPI-0-i-0-m	Non-UAN	*m*-cresol	0	96	2.5	70	6.60	6.31
SPI-0-i-1-m		*m*-cresol	1	103.2	3.9	5,600	7.21	6.86
SPI-0-i-5-m		*m*-cresol	5	118.2	2.4	5,950	8.72	8.32
SPI-0-i-0-d	Non-UAN	DMSO	0	93.8	2.3	67	1.92	1.85
SPI-0-i-1-d		DMSO	1	99	3.8	5,150	2.84	2.72
SPI-0-i-5-d		DMSO	5	105.9	2.1	5,340	3.94	3.77

Samples	Compatibilizer	Solvent	Silica content (wt %)	Tensile strength (Mpa)	Elongation (%)	Hydrolytic stability (hr, 80 °C)[a]	Proton conductivity (10^{-2} S/cm)	
							Before	After
SPI-0-i-0-m	UAN	*m*-cresol	0	96	2.5	70	6.60	6.31
SPI-22-i-1-m		*m*-cresol	1	102.3	7.7	>7000	8.70	measured
SPI-22-o-1-m		*m*-cresol	1	101.4	7.3	>7000	5.84	measured
SPI-0-i-0-d	UAN	DMSO	0	43.8	2.3	67	1.92	1.85
SPI-22-i-1-d		DMSO	1	71.3	8.1	>7,000	2.93	measured
SPI-22-o-1-d		DMSO	1	68.4	7.9	>7,000	1.64	measured
SPI-4-i-1-m	UAN	*m*-cresol	1	101.9	8.2	>7,000	7.24	measured
SPI-13-i-1-m		*m*-cresol	1	103.2	7.9	> 7,000	7.84	measured
SPI-22-i-1-m		*m*-cresol	1	102.3	7.7	> 7,000	8.70	measured
SPI-74-i-1-m		*m*-cresol	1	100.3	7.9	> 7,000	9.98	measured

Dispersion of Carbon Nano Tube Using Amphiphilic Reactive Oligomer



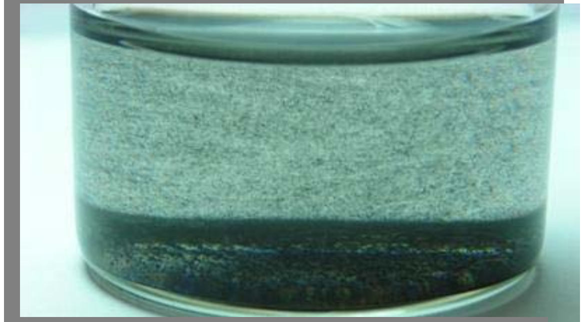
UAN+CNT+NMP (0.05wt% CNT) Not Polymerized

UAN+CNT+NMP (0.05wt% CNT)

CNT+NMP (0.05wt% CNT)

After 3 days

CNT+NMP (0.05wt% CNT)



UAN+CNT+NMP (0.05wt% CNT)