Polymeric and Inorganic Nanoparticles for Environmental Applications

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Nanotechnology + Environmental Technology = “Nanoparticles”

Environmental Pollution Monitoring:
- Nanosensor
  - Ag, Au, Pd, SnO₂
  - ZnO₂, WO₃, TiO₂
  - CdSe
  - Carbon Nano Tube (CNT)

Removal of Environmental Pollutants:
- Magnetic Nanoparticles
- TiO₂ 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]

- SnO₂ (Tin oxide) nanoparticles detecting 3 ppm for CO₂, 15 ppb for NO₂ and O₃, and 50 ppb for NO.
- WO₃ (Tungsten Oxide) based gas sensors to detect H₂S, N₂O, and CO. 5 ppm of H₂S.
- CNTs-FETs for CO, NH₃, NO₂, O₂, and H₂O sensor.
- ZnFe₂O₄ (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 TiO₂ Photocatalyst

1. Japan
   - production of nano-size TiO₂ powder
   - sol containing TiO₂ 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
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
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

- Amphiphilic Reactive Oligomer
- Amphiphilic Oligomer Nanoparticles
- Amphiphilic Crosslinked Polymer Nanoparticles

Nano-dispersion → Crosslinking Polymerization

- 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)

Hydrophobic segment

Hydrophilic segment

APU Nanoparticles

Crosslinked Hydrophobic interior

Mw = 3450 - 7600
Amphiphilic Reactive Oligomer: Urethane Acrylate Anionomer (UAA)

\[ AR = \text{H}_3\text{C} = \text{C} - \text{O} - \text{H}_2\text{C} - \text{H}_2\text{C}^- \]

\[ R_2 = \text{C}_2\text{H}_5 \]

\[ R_1 = \left[ \text{(CH}_2\text{)}_4\text{O} \right]_n \]

\[ M_w = 2350 - 8400 \]

Soap-free emulsification of UAA

Average particle size: 40 - 85nm
Preparation of Amphiphilic Polymer Nanoparticles

1. UAN or UAA
2. Mixing with water
3. Amphiphilic Oligomer Nanoparticles
4. Crosslinking polymerization
5. ACPU or APU Polymer Nanoparticles

Concentration: APU or ACPU nanoparticles in water phase (10 mg – 100,000 mg/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 = 110 mg/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 = 0.1-0.25 mm
  47.6% of sand = 0.25-0.5 mm

Model Pollutant

✓ Model pollutant: phenanthrene (PAH)
  (9-14C, 13.1 µCi/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 = \[\text{HOC}]_s/([\text{HOC}]_w + [\text{HOC}]_{\text{mic}}) \\
   = (\text{mol of HOC sorbed/g of solid})/(\text{mol of HOC in aqueous and micellar solution/L})
2. Extraction efficiency = (desorbed amount of phenanthrene)/(sorbed amount of phenanthrene on aquifer sand) \times 100 (%)
Extraction efficiency of APU particles and Triton X-100 solution

Extraction efficiency = \( \frac{\text{desorbed amount of phenanthrene}}{\text{sorbed amount of phenanthrene on aquifer sand}} \times 100 \, \% \).
Extraction efficiency of ACPU particles and SDS solutions

Extraction Efficiency (%)

Log (SDS or ACPU Particle Dose, mg/L)
In-situ extraction of sorbed phenanthrene from soil using ACPU (APU) nanoparticles and surfactants

Flow rate = 0.01 mL/min
Conc. = 100 mg/L

Fraction of PAH remaining in soil column

Number of Washings (Pore Volumes)
In-situ extraction of sorbed phenanthrene from soil
Using ACPU nanoparticles and SDS solutions

Flow rate = 0.01 mL/min
Conc. = 100 mg/L

Flow rate = 0.01 mL/min
Conc. = 4000 mg/L

Percent mass PAH remaining in soil column

Number of Washings (Pore Volumes)
In-situ extraction of sorbed phenanthrene from soil
Using APU nanoparticles and nonionic surfactants

Flow rate = 0.01 mL/min
Conc. = 100 mg/L

Flow rate = 0.01 mL/min
Conc. = 4000 mg/L
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 structure.
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)

![Diagram of MEUF process](image-url)
NEUF (Nanoparticle-enhanced ultrafiltration)

Amphiphilic nanopolymer particle
Polyaromatic hydrocarbon (PAH)

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

Retentate
Membrane
Permeate
Dead-end stirred cell filtration system

- Feed reservoir
- UF Test Cell
- Magnetic stirrer
- Pressure Gauge
- Electronic valance
- Data recording
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/cm².

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

Amphiphilic Polymer Lab.
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
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 domains:
- 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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Compatibilizer</th>
<th>Solvent</th>
<th>Silica content (wt %)</th>
<th>Tensile strength (Mpa)</th>
<th>Elongation (%)</th>
<th>Hydrolytic stability (hr, 80°C)</th>
<th>Proton conductivity (10⁻² S/cm)</th>
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<tbody>
<tr>
<td>S1-0-i-0-m</td>
<td>Non-UAN</td>
<td>m-cresol</td>
<td>0</td>
<td>96</td>
<td>2.5</td>
<td>79</td>
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Dispersion of Carbon Nano Tube Using Amphiphilic Reactive Oligomer

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

After 3 days

CNT+NMP (0.05wt% CNT)

UAN+CNT+NMP (0.05wt% CNT)