# Nanoparticle Analytical Analysis

Literature Review of Various Analytical Techniques,

2012 Update

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# Current Environmental

- **Whole Effluent Toxicity (WET)**
- **Water or Wastewater Plant Toxicity**
  - **Pass Through**
  - **Finished Drinking Water**
- **Lack of Treatment Options**
  - **Membrane Filtration**
  - **Chemical Precipitation**
- **POTW Digester Sludge Site Toxicity**
  - **Loss of Class A rating**
- **Industrial Pretreatment**
  - **40 CFR 403 Regulations- De Minimis**

# Nanoparticle Industrial Uses

- Material property modification
  - Composites
  - Plastics
  - Metal castings and extrusions
- Electronics
  - Solid state devices
  - LED and Plasma Screens
- Paints
- Cosmetics
- Pharmaceuticals
- Diagnostics

# Current Concerns for Drinking Water Production Plants

- Source Water Protection from the POTW Upstream
- Human Toxicity from Contact or Ingestion
- Endocrine Disruptor
- Drug Efficacy
- Treatment Options
  - Membrane Filtration
  - Ultra Membrane Filtration
  - Chemical Precipitation
  - Bio-Filter

# Digester Sludge

- **Land Application Requirements in 40 CFR 503 are not adjusted for new pollutants.**
- **POTW does NOT want their digester sludge defined as hazardous under 40 CFR 261.**
- **NO GUIDANCE for indirect industrial dischargers**
  - **BMP**
  - **BET**

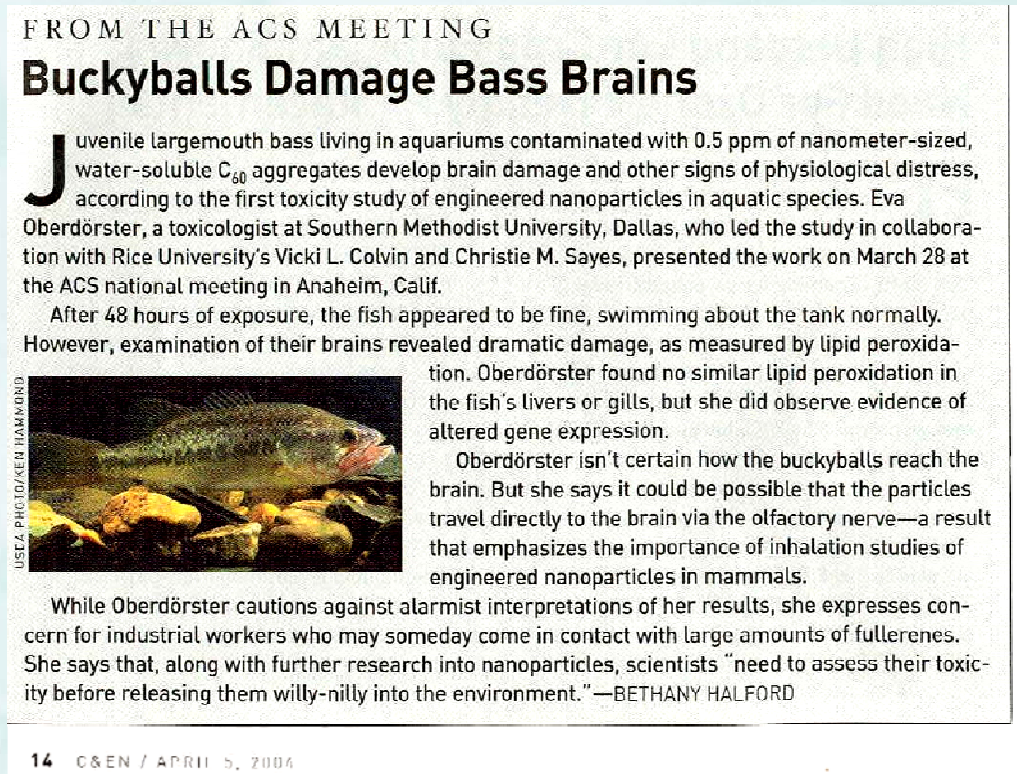
# Industrial Pretreatment

- **No Categorical Standards exist for nanoparticles as a specific pollutant.**
  - **Particle formula, size and toxicity.**
  - **Treatment BMP or BET for direct or indirect dischargers.**
  - **General chemical reactivity for discharge.**
    - **Corrosive, flammable, reactive, color, and odor**
- **Significant Industry Standards have no guidance from Regulatory Agencies.**
  - **Impacts on the treatment works or upon the quality of effluent from the treatment works.**
- **De Minimis Discharger**

# Current State of Affairs with Nanomaterials

# Whole Effluent Toxicity

## C&E News, April 5, 2004



FROM THE ACS MEETING

### Buckyballs Damage Bass Brains

Juvenile largemouth bass living in aquariums contaminated with 0.5 ppm of nanometer-sized, water-soluble $C_{60}$ aggregates develop brain damage and other signs of physiological distress, according to the first toxicity study of engineered nanoparticles in aquatic species. Eva Oberdörster, a toxicologist at Southern Methodist University, Dallas, who led the study in collaboration with Rice University's Vicki L. Colvin and Christie M. Sayes, presented the work on March 28 at the ACS national meeting in Anaheim, Calif.

After 48 hours of exposure, the fish appeared to be fine, swimming about the tank normally. However, examination of their brains revealed dramatic damage, as measured by lipid peroxidation. Oberdörster found no similar lipid peroxidation in the fish's livers or gills, but she did observe evidence of altered gene expression.

USDA PHOTO/KEN HAMMOND

Oberdörster isn't certain how the buckyballs reach the brain. But she says it could be possible that the particles travel directly to the brain via the olfactory nerve—a result that emphasizes the importance of inhalation studies of engineered nanoparticles in mammals.

While Oberdörster cautions against alarmist interpretations of her results, she expresses concern for industrial workers who may someday come in contact with large amounts of fullerenes. She says that, along with further research into nanoparticles, scientists "need to assess their toxicity before releasing them willy-nilly into the environment."—BETHANY HALFORD

14 C&EN / APRIL 5, 2004

# Industrial Secrecy

**GROUPS ENCOURAGE NANOMATERIAL STEWARDSHIP**

**C&E News, July 21, 2008**

- Industry trade groups that represent nanotechnology companies are urging their members to join EPA's voluntary **Nanoscale Materials Stewardship Program (NMSP)**.
  In a joint statement issued on July 14, the American Chemistry Council's Nanotechnology Panel, the Nano Business Alliance, and the Synthetic Organic Chemical Manufacturers Association's Nanotechnology Small & Medium Enterprise Coalition highlighted the importance of the program in helping EPA make informed regulatory decisions about nanomaterials. **"Information collection under the NMSP is a necessary step for EPA to better understand the potential health and environmental effects of nanoscale materials and to determine if any regulatory changes are needed,"** the groups wrote. Since EPA launched NMSP in January 2008, **only four companies** have provided basic information about their nanotech products. The agency expects only **about a dozen** more to do so by the program's July 28 deadline. Initially, EPA expected to receive information from more than **200 firms**. If participation in the pro- gram remains weak, the trade groups warn, EPA is likely to make it mandatory.

1. Altairnano
2. Ahwanee
3. Arkema
4. BASF Corporation
5. Bayer Material Science
6. Dow Chemical
7. DuPont
8. Evonik/Degussa
9. General Electric
10. International Carbon Black Association
11. Nano-C
12. Nanofilm
13. Nanophase Technologies Corporation
14. Nantero
15. Office ZPI
16. PPG Industries
17. Pressure Chemical
18. Quantum Sphere
19. Sabic Plastic Innovations
20. Sasol North America
21. Selah Technologies, Inc
22. SouthWest NanoTechnologies, Inc.
23. Showa Denko KK
24. Silver Nanotechnology Working Group
25. Strem Chemicals
26. Swan Chemicals Inc.
27. Synthetic Amorphous Silica and Silicate Industry Association
28. Unidym
29. Three companies claimed as Confidential Business Information

## EPA's voluntary Nanoscale Materials Stewardship Program (NMSP) ended in December 2009

**http://epa.gov/oppt/nano/stewardship.htm**

- **The Agency released its Interim Report on the NMSP (PDF) (38 pp, 872K) in January 2009 and will issue a final report in 2010. (Note: No Final Report)**
- **To address these gaps and prevent potential risks that may be posed by nanoscale materials, EPA is taking a number of regulatory actions under the Toxic Substances Control Act.**

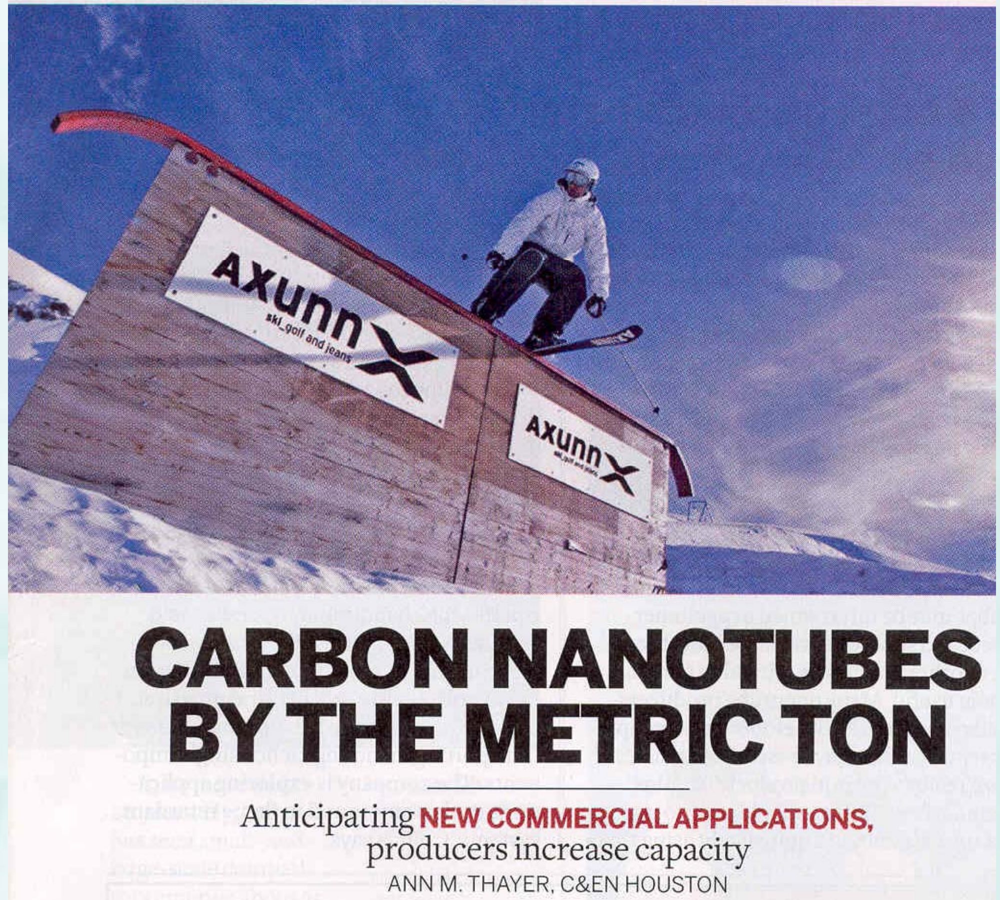
**The WPMN has identified a representative list of manufactured nanoscale materials for environmental health and safety testing, including:**

- **fullerenes ($C_{60}$)**
- **single-walled carbon nanotubes (SWCNTs)**
- **multi-walled carbon nanotubes (MWCNTs)**
- **silver nanoparticles**
- **iron nanoparticles**
- **carbon black**
- **titanium dioxide**
- **aluminum oxide**
- **cerium oxide**
- **zinc oxide**
- **silicon dioxide**
- **polystyrene**
- **dendrimers**
- **nanoclays**

**The OECD has established a Working Party on Manufactured Nanomaterials (WPMN) that is engaged in a variety of projects to further our understanding of the properties and potential risks of nanomaterials:**

- **OECD/NNI International Symposium on Assessing the Economic Impact of Nanotechnology Background Paper 4 - Models, Tools and Metrics Available to Assess the Economic Impact of Nanotechnology**

# So, Here They Come!


CARBON NANOTUBES BY THE METRIC TON

Anticipating **NEW COMMERCIAL APPLICATIONS,** producers increase capacity

ANN M. THAYER, C&EN HOUSTON

# Analytical Problems

- **Nanoparticles are defined by:**
  - Size
    - 1 nm-200 nm
    - Metallic, molecular, atomic
  - Shape
    - Spherical
    - Prismatic
    - Rods
  - Surface Treatment
    - Uncapped
    - Capped
- **None of these characteristics are defined by EPA tests**

# Nanoparticle Terms

- **Phonon: A quantum of vibrational or sound energy in a crystal lattice or solid: often characterized as being heat energy.**
- **Plasmon: The quasiparticle resulting from the quantization of oscillations from phonons.**

# Nanoparticle  Physics (cont.)

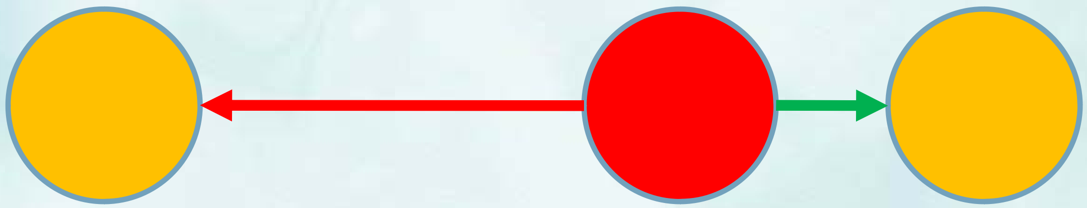
- More recently surface plasmons have been used to control colors of materials.
- This is possible since controlling the material's surface shape controls the types of surface plasmons that can couple to it and propagate across it. This in turn controls the interaction of light with the surface.

# Detection Physics

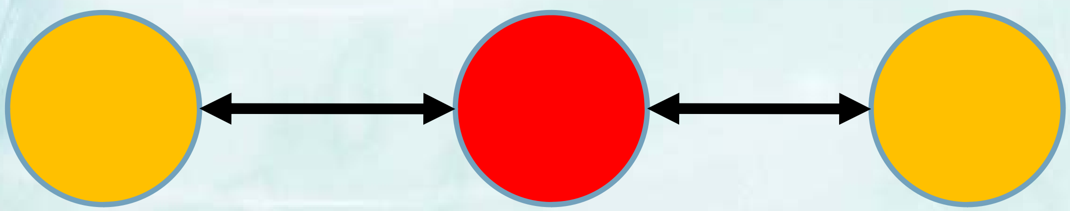
- **Nanoparticle bond vibration interactions with probe source.**
- **Scattering phenomenon of probe energy.**
- **Molecular orbital formation.**
  - **Plasmon**
- **Molecular orbital transitions.**
  - **Phonon**
- **Luminescence of excited states.**
- **UV-vis Absorbance.**
- **Electrochemical Redox**
  - **(Reversible or Irreversible)**

# Molecular Vibrations

## Asymmetric Vibration

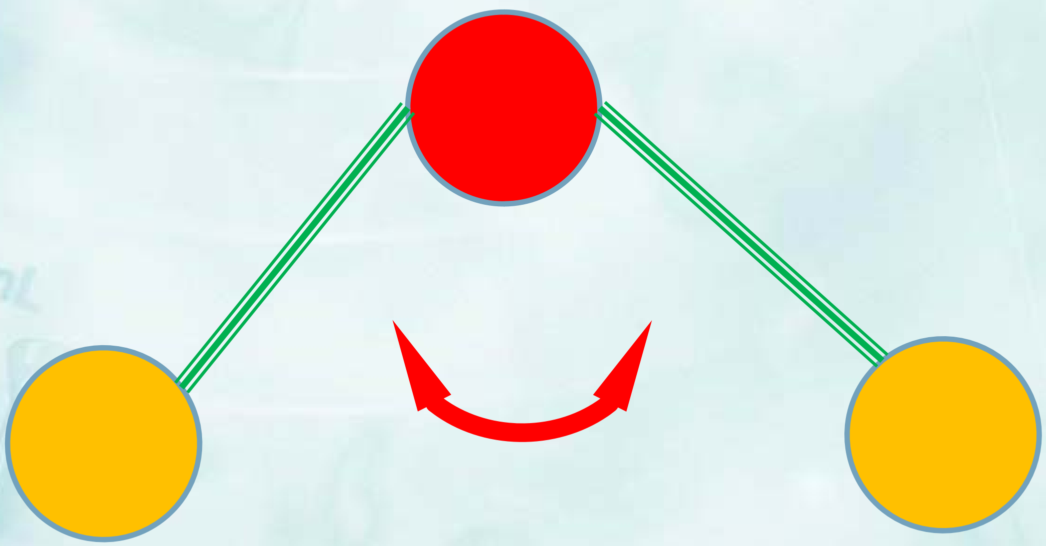


## SymmetricVibration

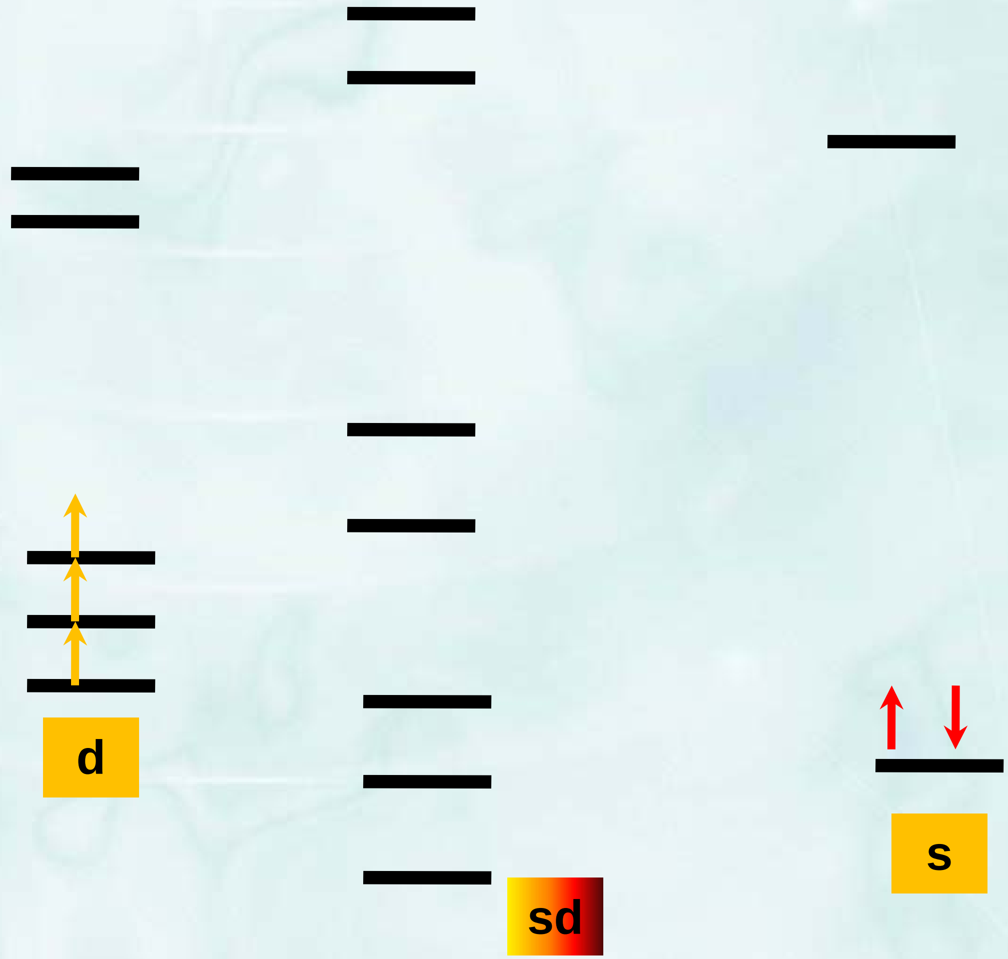


# Molecular Vibrations

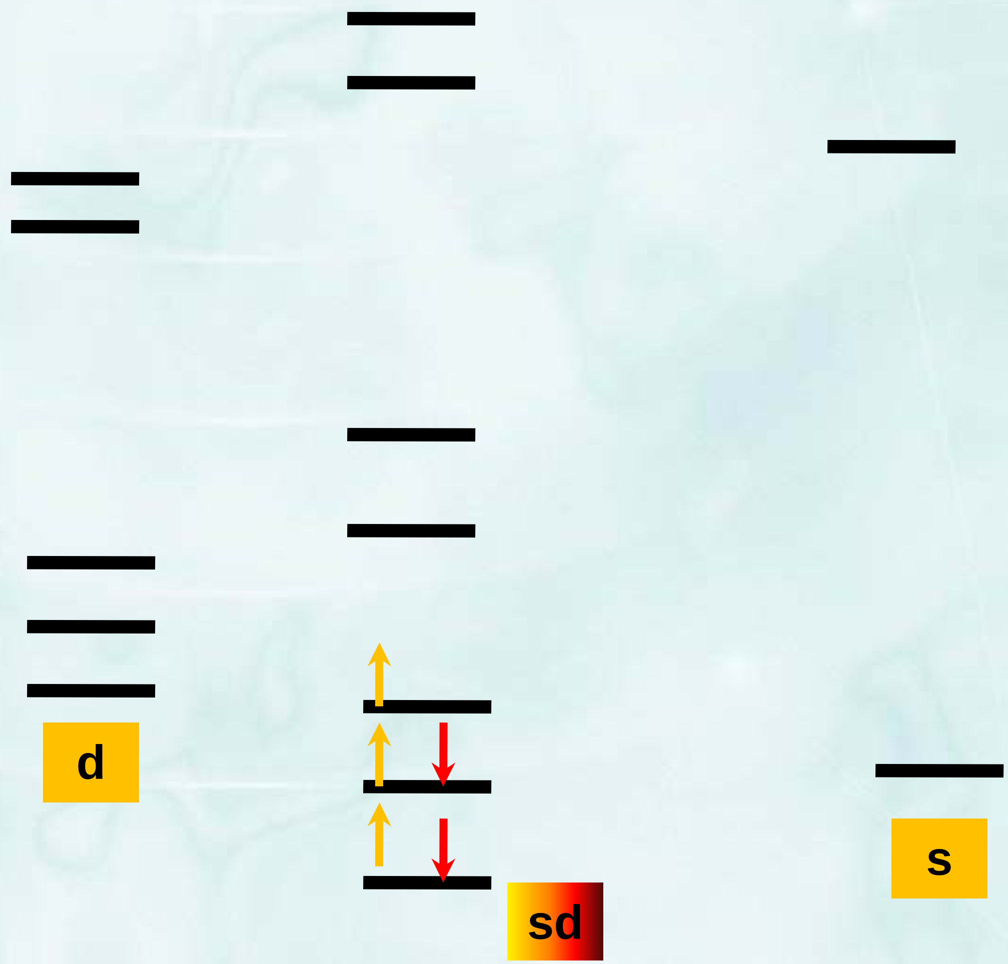
## Bend or Scissor Vibration



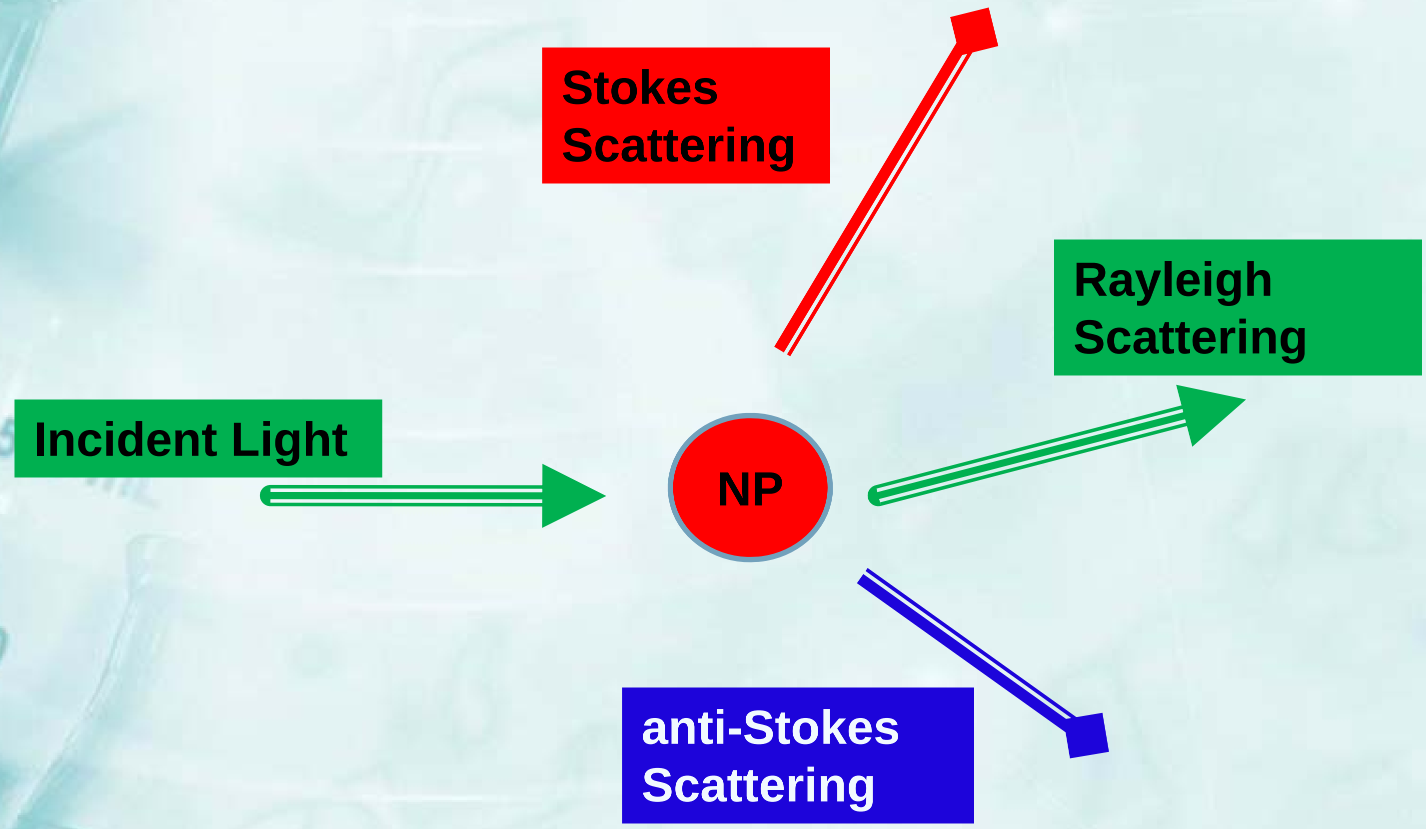
# Molecular Orbital Formation



# Molecular Orbital Formation



# Raman Scattering



# Particle Size Raman Influence

**Meier (2006)**

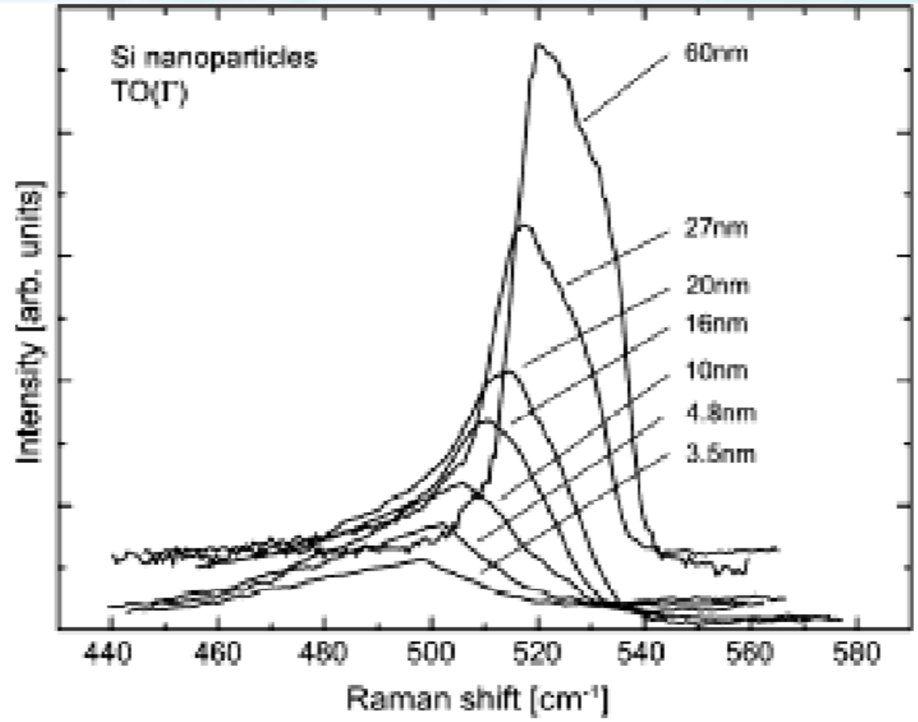
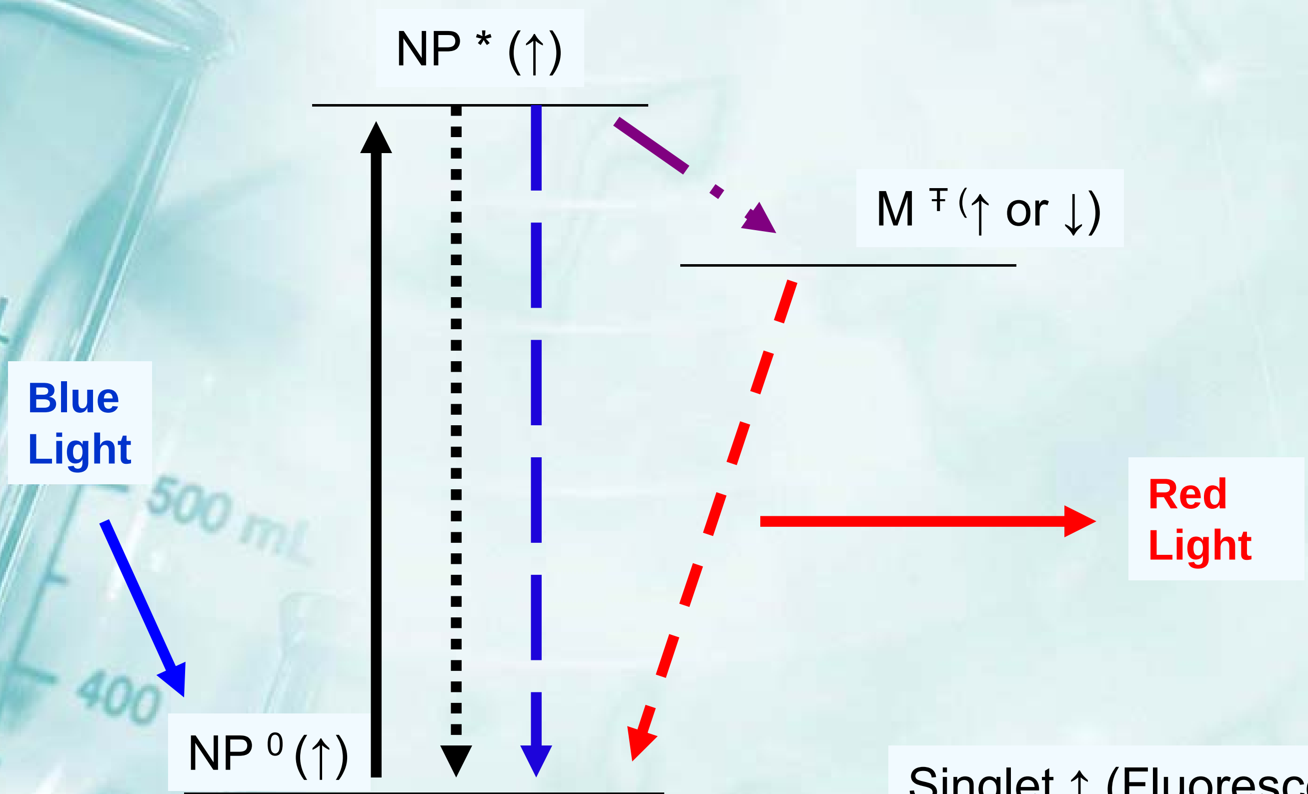



Fig. 2. First-order Raman spectra for silicon nanoparticles with BET diameters between 3.5 and 60nm.

# Photo Luminescence




Singlet ↑ (Fluorescence)
Triplet ↓ (Phosphorescence)

# Nanomaterial Luminescence Fe/Zn Ratios 15% to 40%

**Jin (2008)**

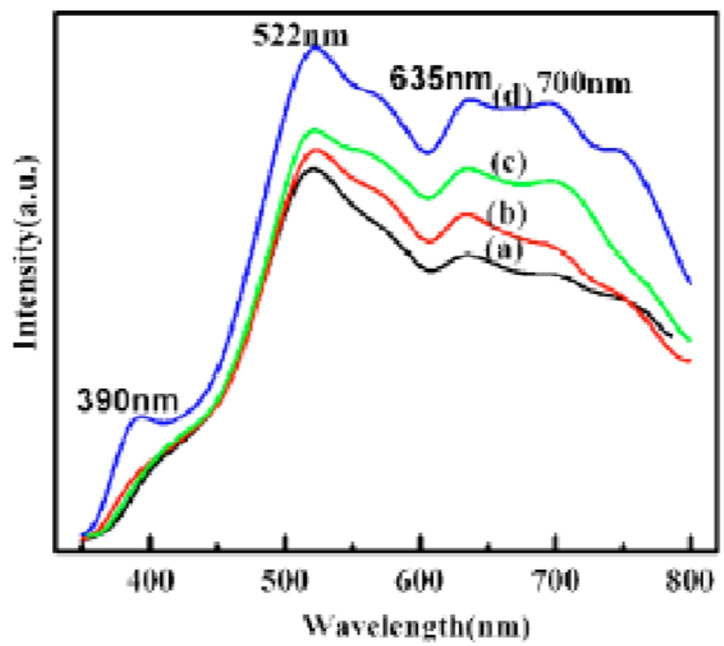
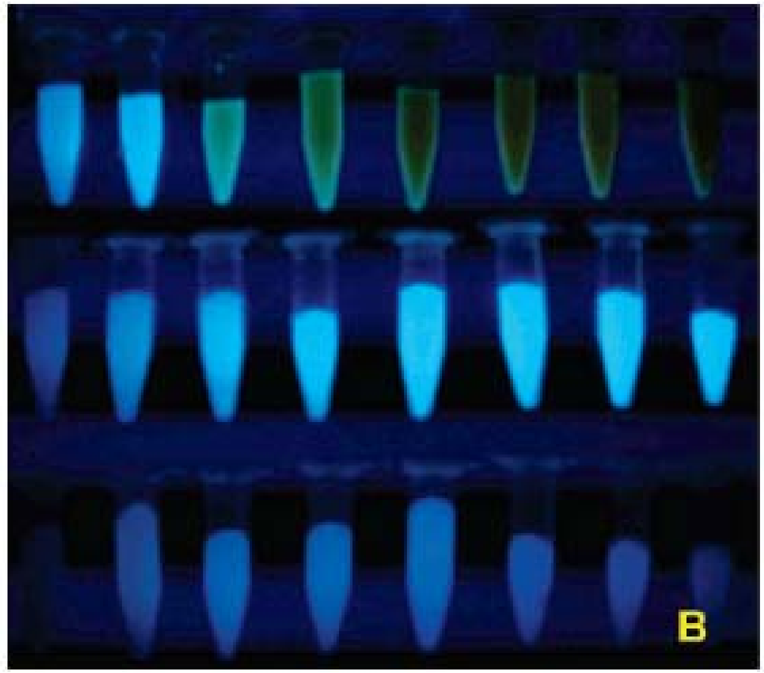



FIG. 4. (Color online) PL spectra of samples acquired at RT: (a) F/Z-15, (b) F/Z-20, (c) F/Z-30, and (d) F/Z-40.




**Images of Silica NPs prepared with varying percentages (3-80%) of APTS and heated at different temperatures. (B) 300 nm UV illumination**

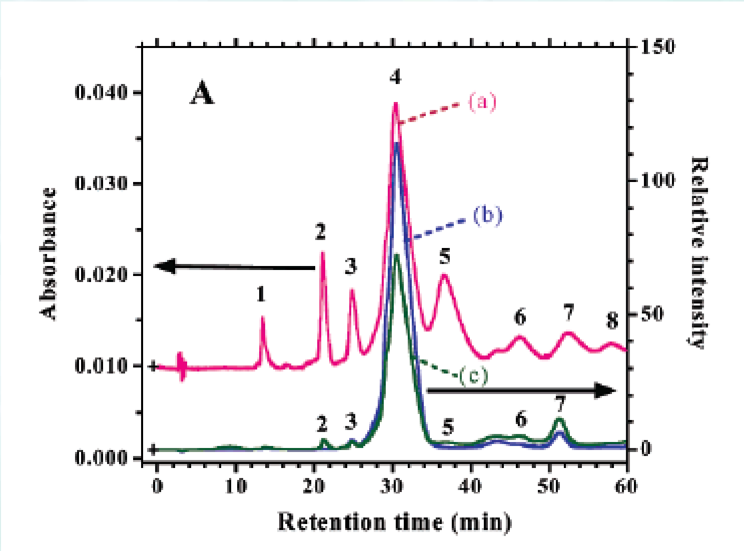
**The concentration of NPs is 10 mg/mL in DI water.**

**Wang (2008)**

# UV-vis Absorbance / Luminescence

## Choi (2006)

**$Au_{75}$ MPC**

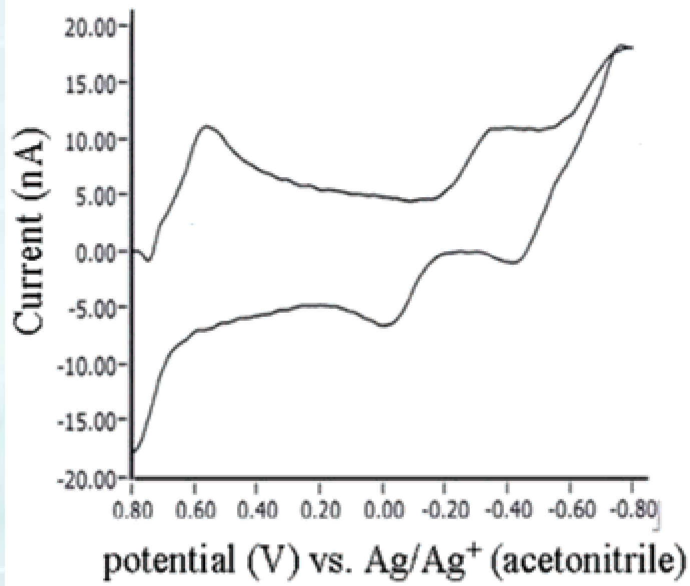


# Electrochemical Redox By CV

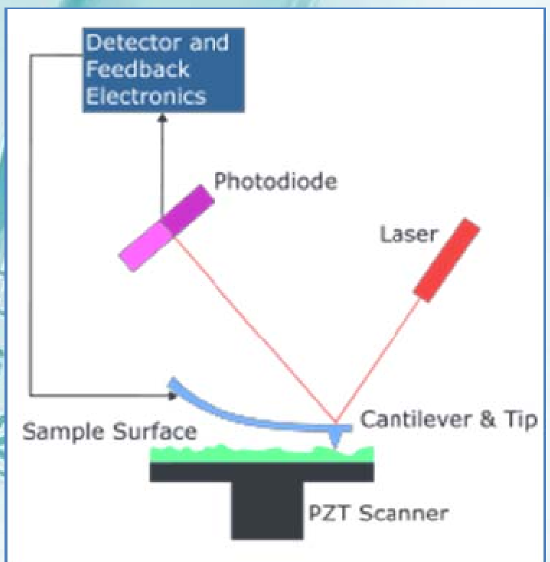
## Song (2004)

**Au$_{38}$ MPC**

**CV** of peak * after background subtraction

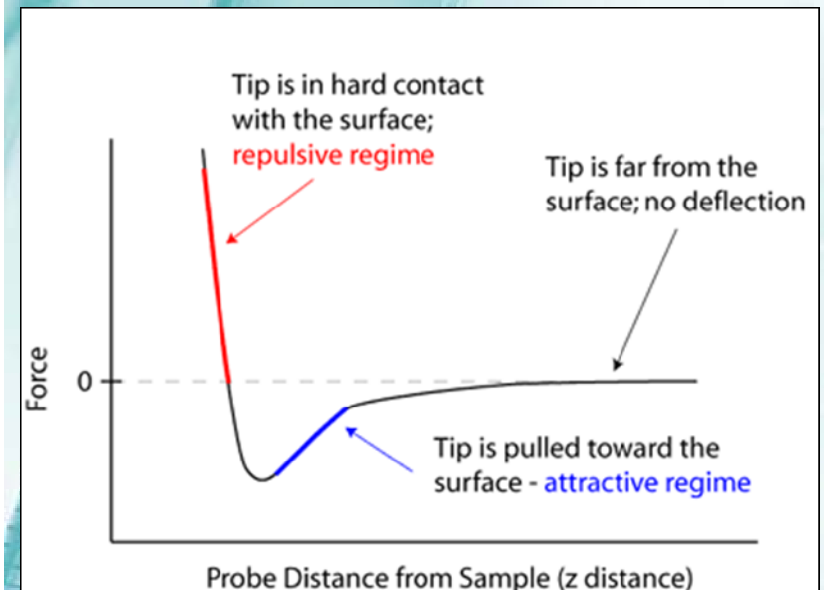


# Atomic Force Microscopy




**AFM Probe Deflection**

**Today, most AFMs use a laser beam deflection system, introduced by Meyer and Amer, where a laser is reflected from the back of the reflective AFM lever and onto a position-sensitive detector. AFM tips and cantilevers are microfabricated from Si or $Si_3N_4$. Typical tip radius is from a few to 10s of nm**




# Measuring forces

Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging.
The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever.
Hook's law gives F = -kz, where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent

# Separation and Purification Methods and Technology

# Examples

- Filtration
- Dialysis
- Centrifugation
- Size Exclusion Chromatography
- Ion Pair Reverse Phase HPLC

# Examples of Analyses

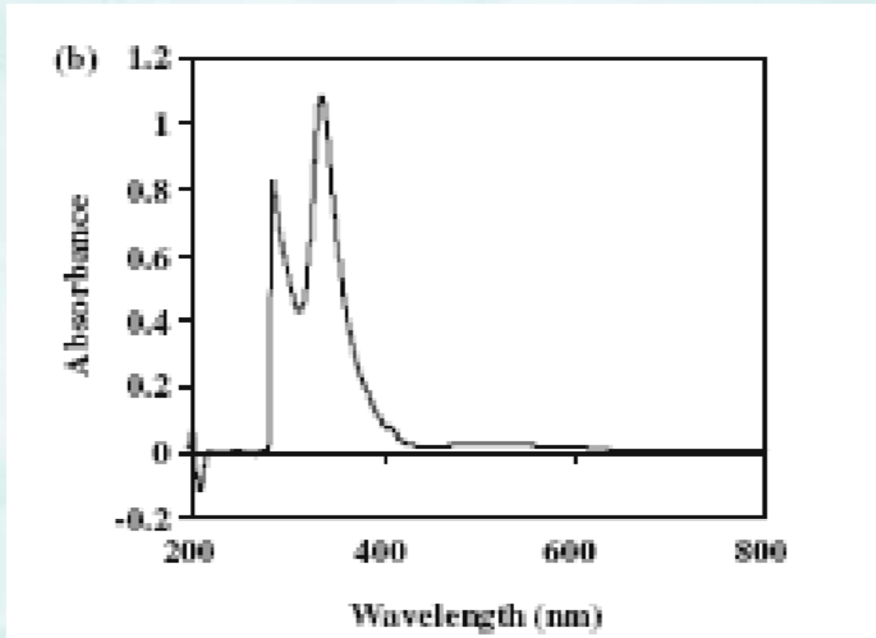
**No Water or Wastewater**

# Filtration

**Cheng (2005)**

- **Nano-$C_{60}$ in DI water cannot be extracted from its aqueous suspension with either toluene or benzene.**
- **However, addition of an electrolyte, e.g.,2 wt% NaCl, will precipitate $C_{60}$ from its aqueous dispersion**

The absorption spectra showed clear $C_{60}$ characteristic peaks at **336** nm and **407** nm



# Centrifugation and Size Exclusion Chromatography

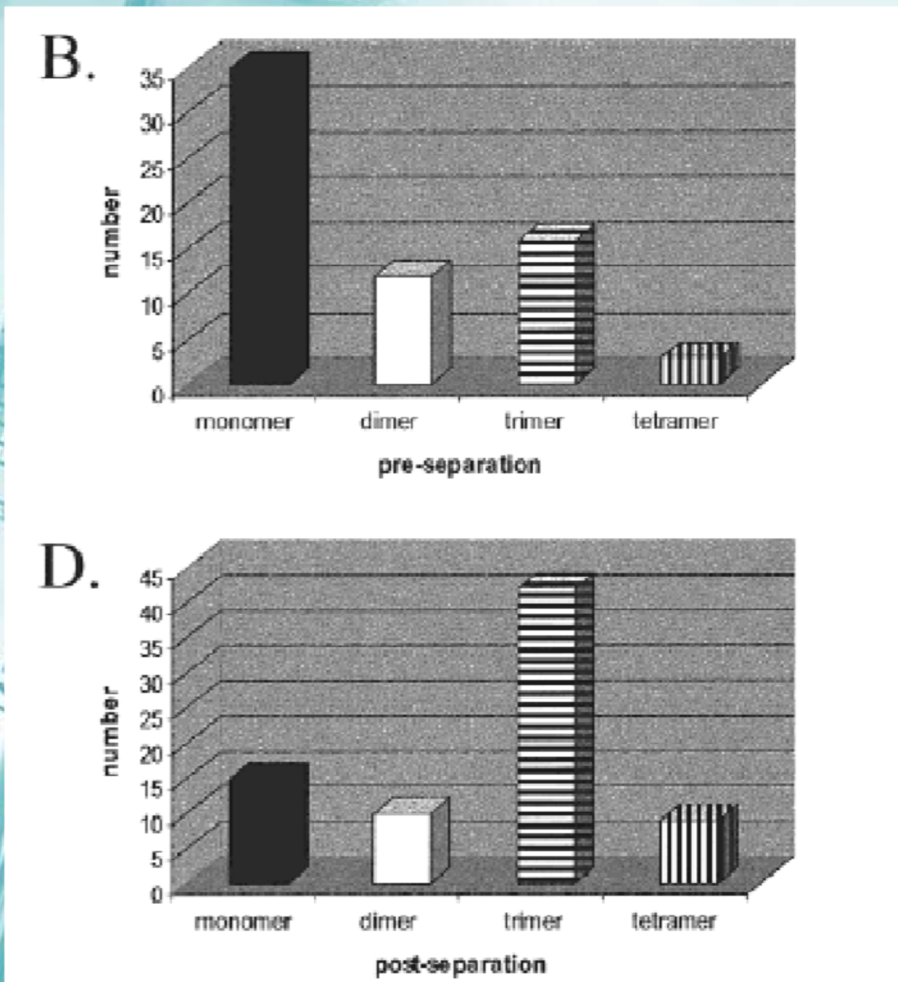
**Novak (2001)**

- bis(p-sulfonatophenyl)phenylphosphine (BSPP)
- Ligand exchange was accomplished by adding 1 mg/mL of the disodium BSPP salt to the nanoparticle array suspension and stirring for 4 h.
- The water-soluble BSPP-capped nanoparticle array mixture was centrifuged in 1M aqueous sucrose solution.

- Purifying gold nanoparticles by size exclusion chromatography has the same complications as centrifugation plus the additional problem of irreversible adsorption to the stationary phase.
- This was prevented by using an aqueous mobile phase containing 40 mM sodium dodecyl sulfate (SDS) buffer, as described by Wang and coworkers for purifying metal nanorods.
- The size exclusion chromatography contained a Waters UK6 injector, 590 programmable solvent pump,

- and Rainin Dynomax UV-C single wavelength UV-vis detector set at 525 nm ($\lambda_{max}$ for the single particle plasmon absorbance).
- A 500- and a 350-Å pore diameter silica microsphere GPC column were mounted in series (Alltech, Inc.).
- Injection volumes were 25 μL for all samples studied.

# Results



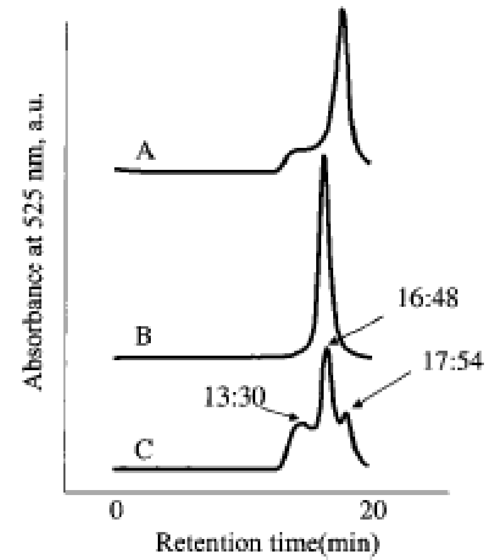




**Figure 4.** Chromatogram showing retention times of (a) 10-nm-diameter gold monomers, (b) 30-nm-diameter gold monomers, and (c) a 1:1 mixture of 10- and 30-nm-diameter gold monomers.

# Ion Pair Chromatography

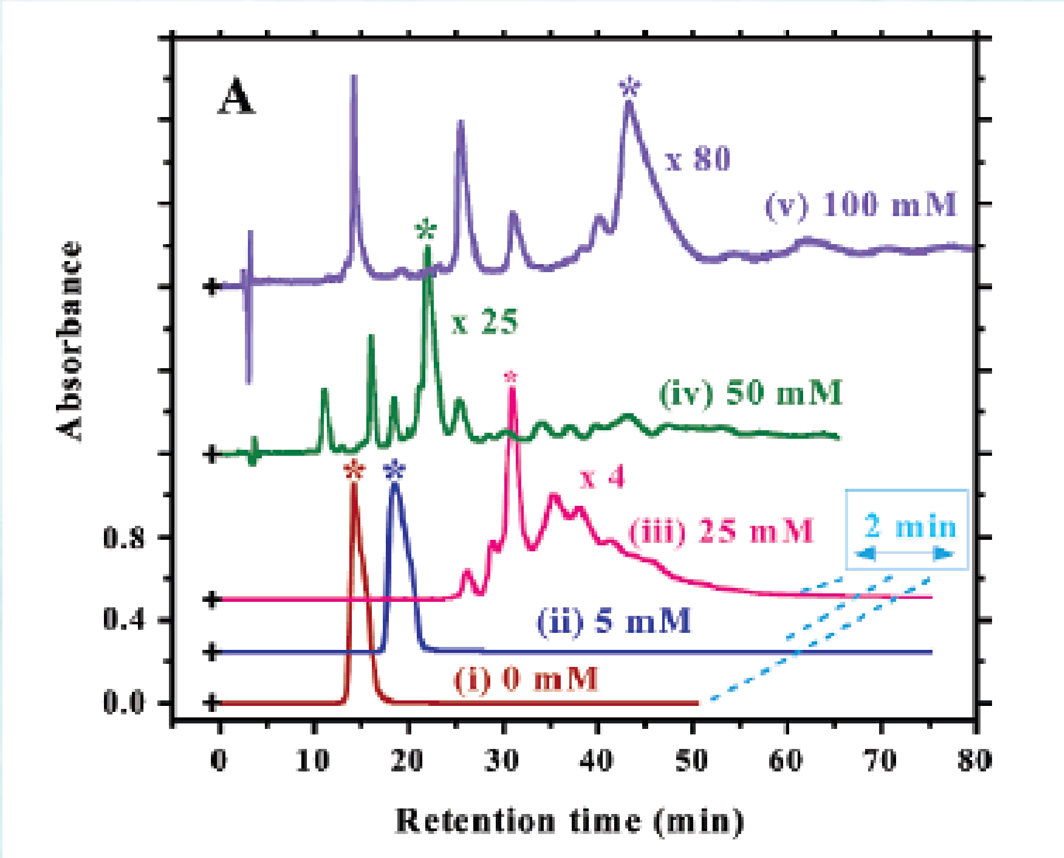
Choi (2006)

- **Au Monolayer Protected Clusters**
- **The chromatography was carried out with a Waters (Milford, MA) instrument consisting of a model 600 controller pump capable of gradient elution; a model 2996 PDA and a model 2475 multiwavelength fluorescence detector.**
- **PDA spectra (<u>1.2 nm resolution</u>) were taken over 250-800 and 280-800 nm for N-acetyl-L-cysteine MPC and tiopronin MPC eluates, respectively,**

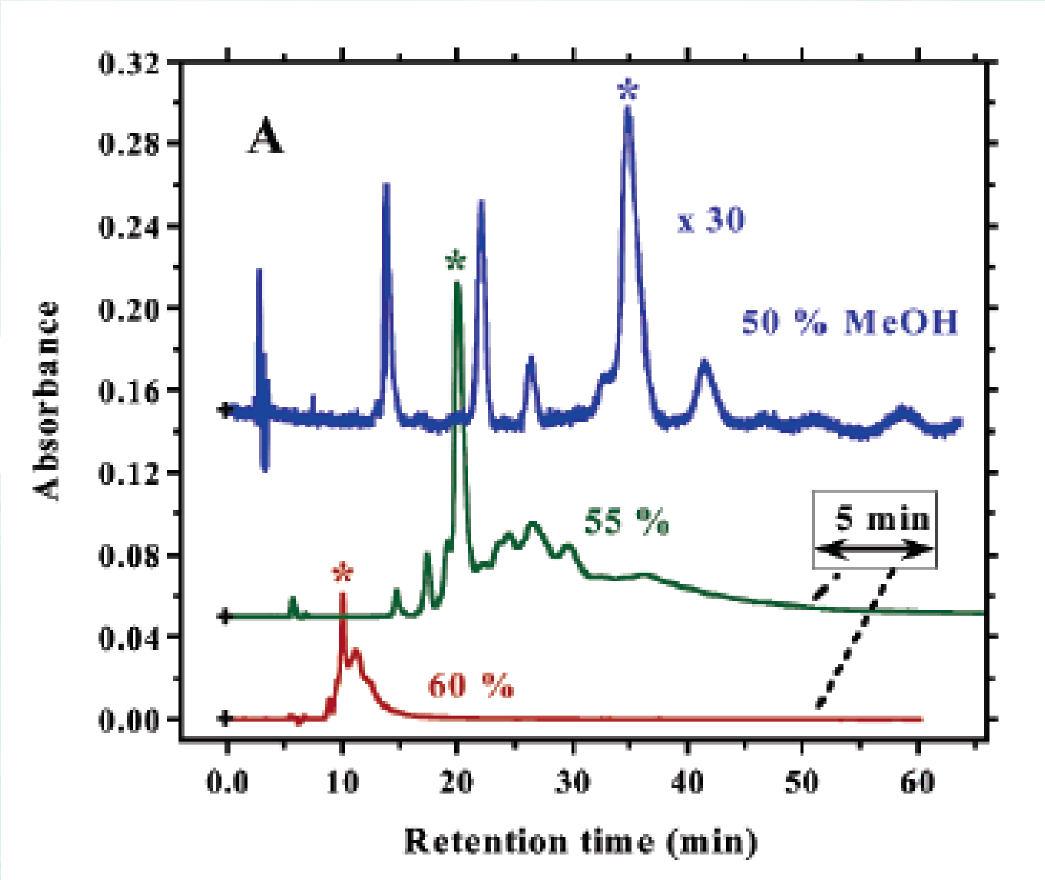
- whereas fluorescence (10-nm resolution) was monitored respectively at 540-740 and at 580-780 nm, exciting at 400 nm.
- The chromatographic column (150  4.6 mm i.d. stainless steel) was packed with 5-μm C18 bonded silica with 300-Å pore size (BioBasic-18, Thermo Electron Corp., Bellefonte, PA).
- The mobile phase contained $Bu_4N^+F^-$ as ion-pairing reagent, MeOH as organic modifier, and phosphate buffer.

# Results

**Ion Pair Concentration**

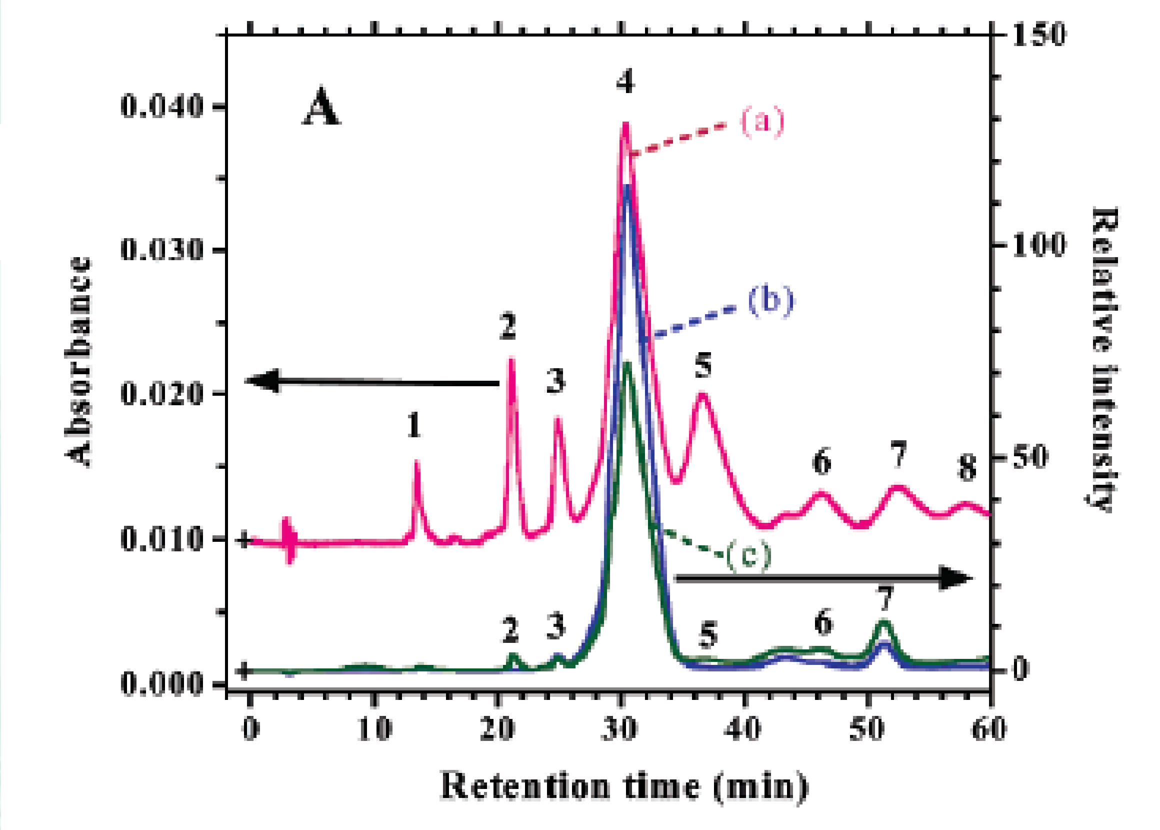


MeOH Concentration



Separation on the C18 column using a mobile phase (1:1) MeOH/0.025 M, pH 4.5, phosphate buffer containing 55 mM [$Bu_4N^+F^-$] (a), pink absorbance chromatogram detected by PDA at 400 nm (offset for clarity) and (b) blue and (c) green, fluorescence detection at 640 and 720 nm, respectively, with excitation at 400 nm.

**Absorbance & Luminescence**



# Water

## Finally, But not Nanoparticles Yet

# Dendrimer Enhanced Ultrafiltration. 1. Recovery of Cu(II) from Aqueous Solutions Using PAMAM Dendrimers with Ethylene Diamine Core and Terminal $NH_2$ Groups, Diallo, ES&T, 2005

- Ultracel Amicon YM regenerated cellulose (RC) and PB Biomax polyethersulfone (PES) membranes from Millipore were evaluated in this study.
- The RC and PES membranes had a diameter of 25 mm with molecular weight cutoff (MWCO) of 5000 Da (5 kDa) and 10 000 Da (10 kDa). For the UF measurements of dendrimer retention in aqueous solutions, the concentrations of the G3-NH2 ($2.42265 \times 10_{-5}$ mol/ L), G4-NH2 ($8.49762 \times 10^{-6}$ mol/L), and G5-NH2 (5.31808 × 10-6 mol/L) PAMAM dendrimers were kept constant in all experiments. Dendrimer concentrations in the feed and permeate solutions were measured using a Shimadzu model 1601 UV-visible spectrophotometer at a wavelength of 201 nm.

- The efficiency of PEUF-based processes for treatment of water contaminated by metal ions will depend on several factors including:
  - (i) polymer binding capacity and selectivity toward the targeted metal ions;
  - (ii) polymer molar mass and responsiveness to stimuli such as solution pH;
  - (iii) polymer sorption tendency onto UF membranes;
  - (iv) polymer stability and toxicity.
- An ideal polymer for PEUF treatment of water contaminated by metal ions should be highly soluble in water and have a high binding capacity/selectivity toward the targeted metal ions along with a low sorption tendency toward UF membranes.

# Detection of Heavy Metal Ions in Drinking Water Using a High-Resolution Differential Surface Plasmon Resonance Sensor, Forzani, ES&T, 2005

- We have built a high-resolution differential surface plasmon resonance (SPR) sensor for heavy metal ion detection. The sensor surface is divided into a reference and sensing areas, and the difference in the SPR angles from the two areas is detected with a quadrant cell photodetector as a differential signal.
- In the presence of metal ions, the differential signal changes due to specific binding of the metal ions onto the sensing area coated with properly selected peptides, which provides an accurate real-time measurement and quantification of the metal ions.

# Conclusion

- **No current research is published on environmental methods for:**
- **sample collection,**
- **Preservation**
- **separation,**
- **quantification  of nanoparticles in water and wastewater matrixes.**

# Suggested Solutions

- **Formation of Standard Methods  Joint Task Group to:**
  - **Compile,**
  - **Review and**
  - **test methods for nanoparticle analysis in matrixes of concern.**
- **Transfer knowledge to regulators**

# Questions