

Dept. of Chemistry and Physics



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# **Nanoparticle Mediated Photodefluorination Monitored by F-19 NMR**

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## What Are Nanoparticles

- Microscopic particles measured in nanometers
- They are the smallest solids that can be manufactured
- Do not behave like classical particles, exist in the world of quantum physics.
- Can have very different atomic and molecular properties such as conductivity, hardness, and melting points than bulk materials.

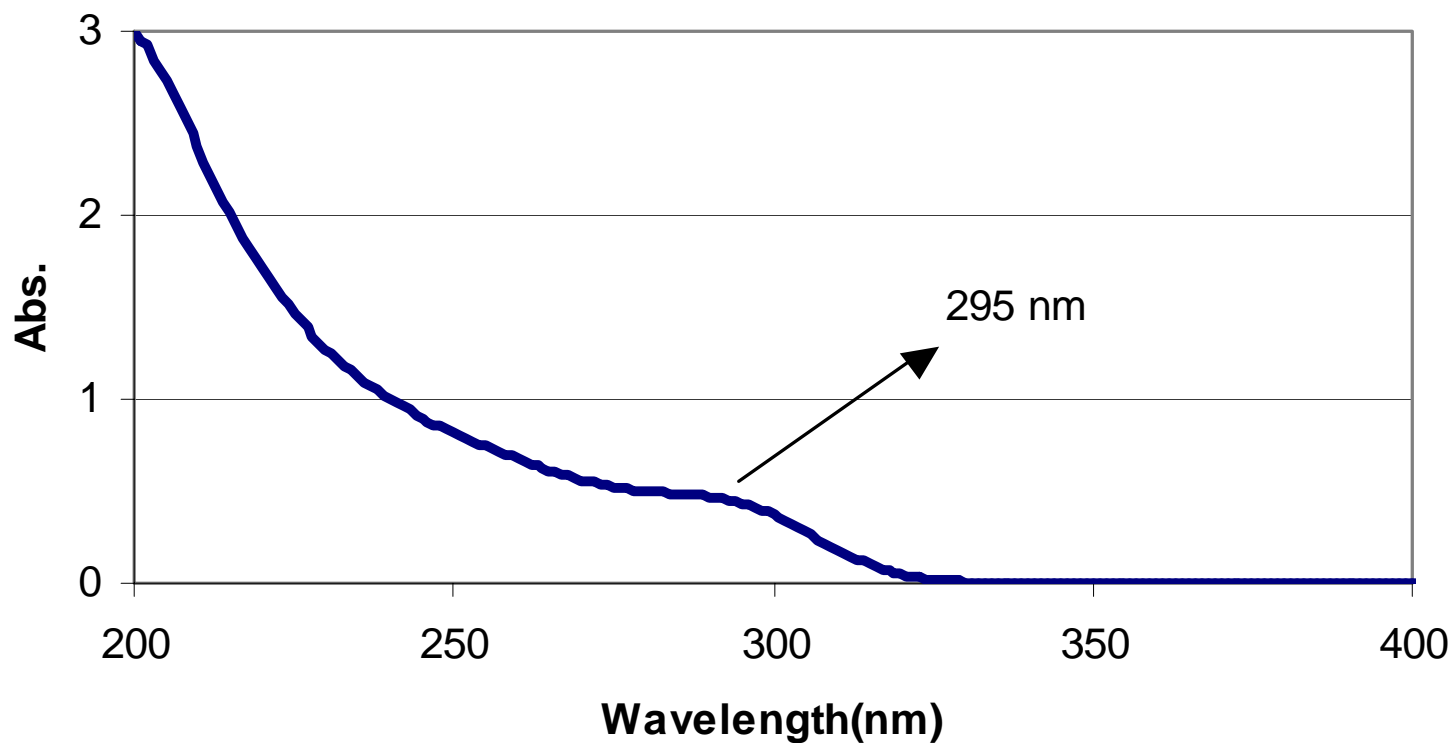


## Preparation of ZnS

- 10 g of sodium polyphosphate was dissolved in 80 mL of deionized water in 200 mL of beaker
- 10 mL of 1.0 M  $\text{Zn}(\text{Ac})_2$  was added with stirring
- 10 mL of 0.85 M  $\text{Na}_2\text{S}$  was also added in one portion
- After mixing for 5 minutes, the solution is centrifuged @ 3500 RPM for 10 minutes
- The solution was decanted, the solid was washed and centrifuged again. 250 mL of water was added to suspend the particles for further experiments



## ZnS UV-Vis Spectra





## Particle Size Calculation – Brus Equation

$$E_{np} = E_g + \frac{h^2}{8r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 r}$$

$E_{np}$  is calculated from the excitonic absorption peak of the nanoparticle, in J

$E_g$  is calculated from the known bulk semi-conductor band gap, in J

For ZnS = 3.68eV

For CdS = 2.40eV

$r$  is the radius of the nanoparticle, in meters

$m_e^*$  is the effective mass of the electron,  $m_e$  is the mass of an electron, in kg

For ZnS = 0.25 $m_e$

For CdS = 0.21 $m_e$

$m_h^*$  is the effective mass of the electron,  $m_h$  is the mass of an electron, in kg

For ZnS = 0.60 $m_e$

For CdS = 0.80 $m_e$

$e$  is the charge on the electron, in C

$\epsilon$  is the dielectric constant of material

For ZnS, 8.3

For CdS, 5.6

$\epsilon_0$  vacuum permittivity constant, in C<sup>2</sup>J<sup>2</sup>M<sup>-1</sup>





## Nanoparticle Photocatalysis with Halogenated Aromatics

-Halogenated aromatics are on EPA priority pollutant list (pentachlorophenol, etc.)

-Can ZnS nanoparticles facilitate the degradation of halogenated aromatics?

$h\nu$

Our system:





## Photodefluorination Experiments

- Use ZnS nanoparticles and excite using 295 – 350 nm
- ZnS nanoparticle  $< 4.0 \times 10^{-5}$  M, 12.5 mM fluoro cpd

• **Table.**  $^{19}\text{F}$  Chemical Shifts (ppm vs.  $\text{CFCl}_3 = 0.0$ ) in  $\text{H}_2\text{O}$  .

<u>Compound</u>	<u><math>\delta F</math></u>
• fluoride (aqueous)	-119.4
• 2-fluorophenol	-137.8
• 3-fluorophenol	-112.7
• 4-fluorophenol	-125.1
• 2-fluorobenzoic acid	-115.4
• 3-fluorobenzoic acid	-113.7
• 4-fluorobenzoic acid	-109.4



# $^{19}\text{F}$ Spectra of 4-fluorophenol (-125.1 ppm) $t = 0$

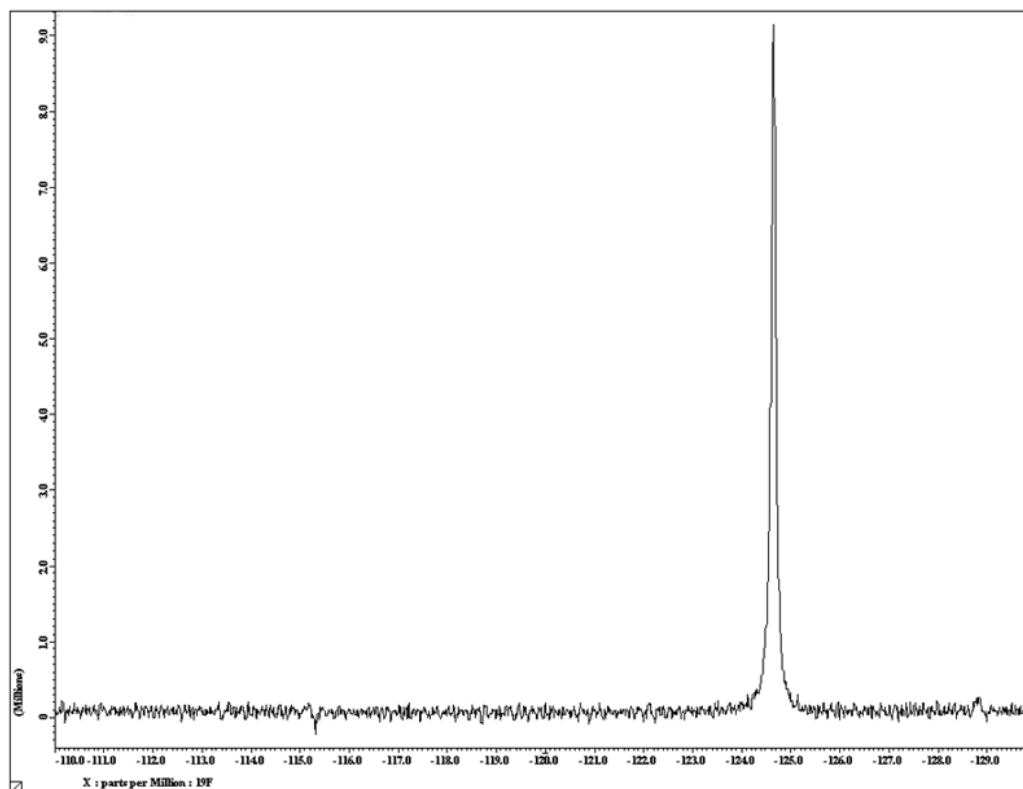


Figure 2a. NMR spectra of 4-fluorophenol in  $\text{H}_2\text{O}$  at  $t = 0$



# $^{19}\text{F}$ Spectra of 4-fluorophenol (-119.4 ppm) Degradation, $t = 24$ h

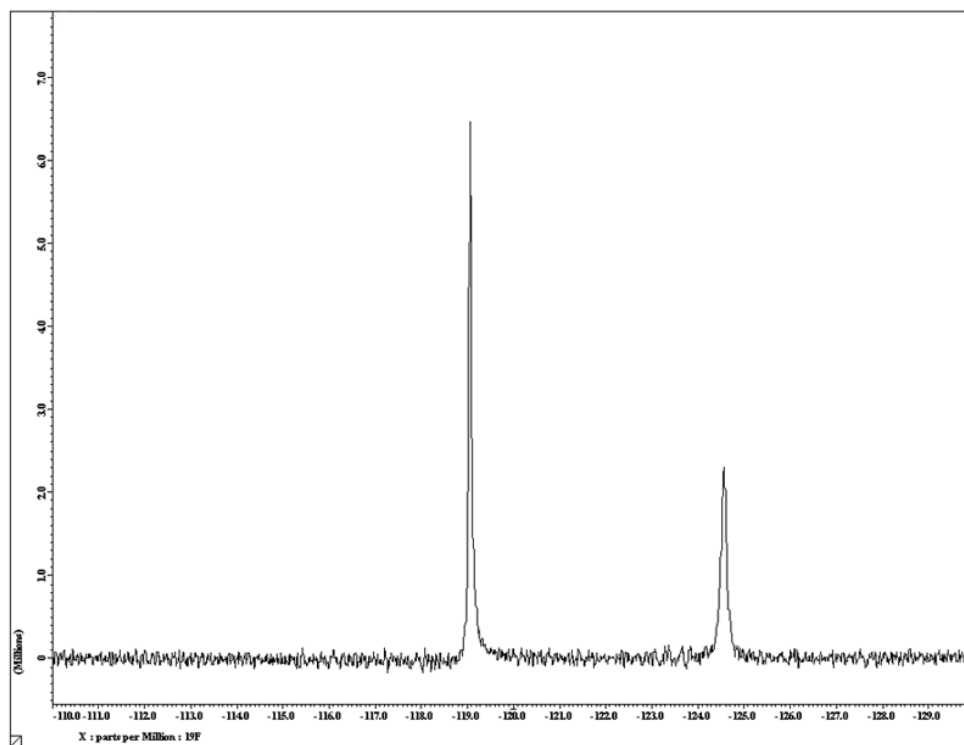
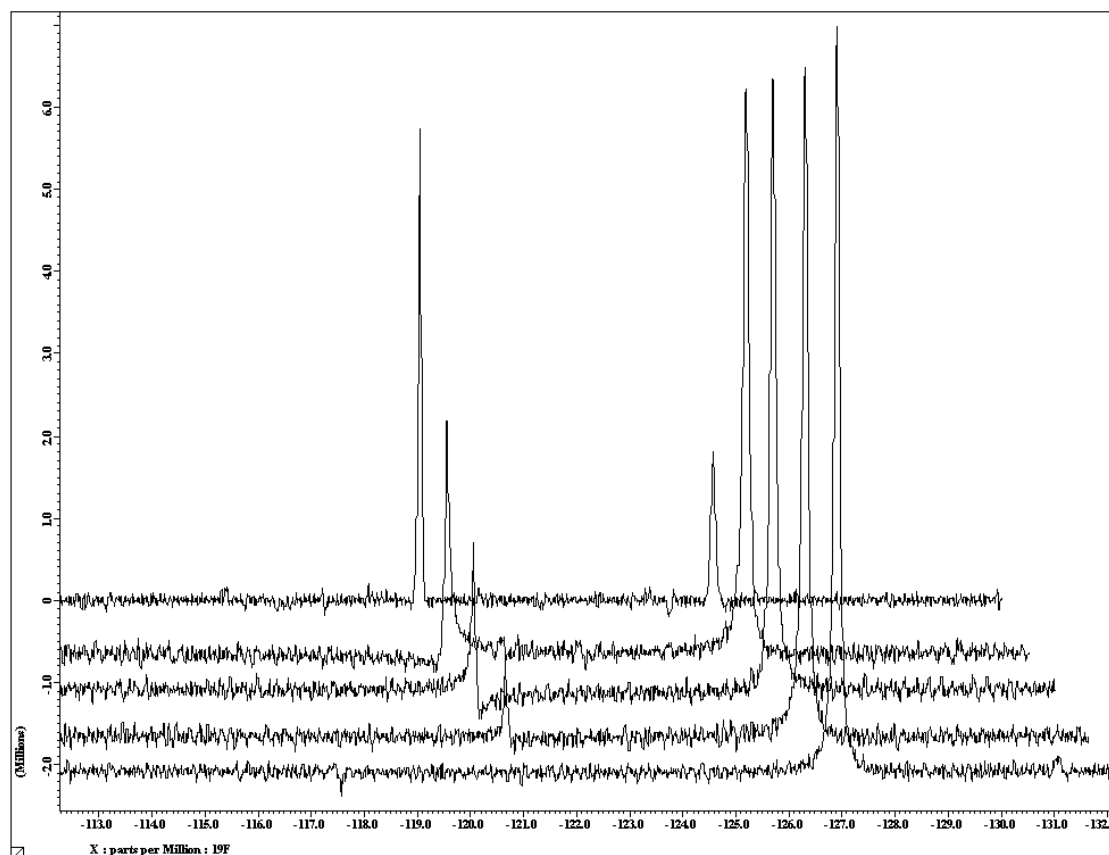


Figure 2b. NMR spectra of 4-fluorophenol in  $\text{H}_2\text{O}$  at  $t = 24$  hours

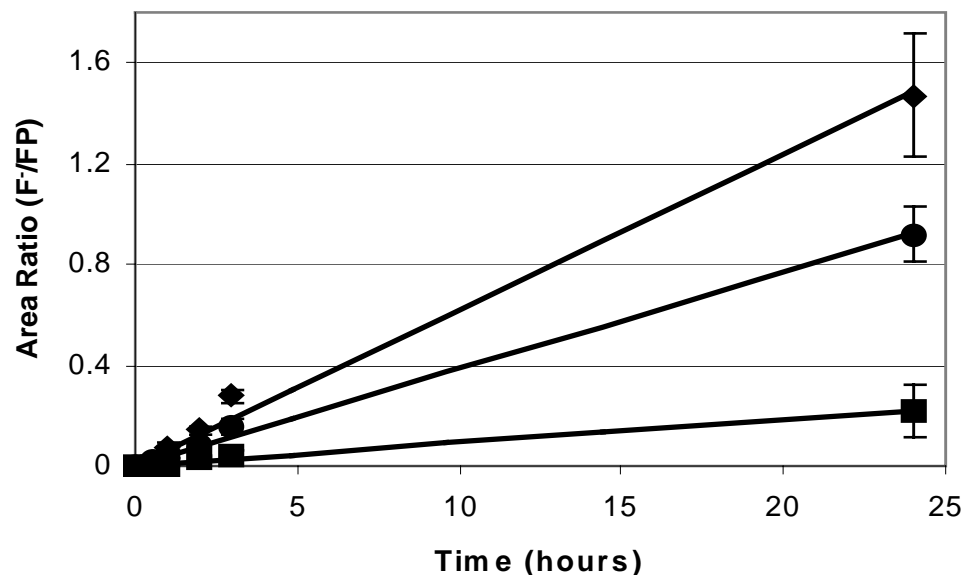


# $^{19}\text{F}$ spectra of 4-fluorophenol Photodegradation $t = 0, 1 \text{ h}, 2 \text{ h}, 3 \text{ h}$ and $24 \text{ h}$ .





# Time Course of 2, 3, and 4-fluorophenol Degradation



**Figure 4.** Increase in fluoride production relative as a function of irradiation time for the 2-, 3-, and 4-fluorophenol systems (circles, squares and diamonds respectively).





# Actinometry

Use standard actinometry procedures to quantify the amount of light impinging on a sample

Measures amount of light absorbed by a sample system

Relative measurement as compared to a known oxalate actinometer with quantum efficiency of 0.57

Standard method that allows you to compare your data to other researchers data



# Actinometry -Procedure

## Standardization of Potassium Permanganate

1. 0.5 mM  $\text{KMnO}_4$  standardized against  $\text{Na}_2\text{C}_2\text{O}_4$  in 10 mL 1M  $\text{H}_2\text{SO}_4$
2. Mix 10 mL of 0.01 M oxalic acid & 0.01 M uranyl nitrate in dark
3. Measure 1 mL and repeat three times under lamp and in the dark for 1 hour;
4. Samples were titrated with standard  $\text{KMnO}_4$  dropwise until persistent pink appeared.
5. Amount of oxalate consumed is related to number of photons absorbed by the sample from the equation

$$\Phi = \frac{\textit{Before}_{(moles)} - \textit{After}_{(moles)}}{X}$$

Where  $\Phi$  is the quantum efficiency of the oxalate actinometer, 0.57



## Titration Data

# Samples	Dark		ZnS		MoS2		CdS	
	KmnO4(mL)	mol C2O4	KmnO4(ml)	mol C2O4	KmnO4(ml)	mol C2O4	KmnO4(ml)	mol C2O4
#1	5.4mL		2.5mL		5.2mL		3.0mL	
#2	5.3mL		2.4mL		5.1mL		2.1mL	
#3	5.4mL		2.5mL		5.5mL		3.5mL	
Average	5.367mL	6.7E-6mol	2.47mL	3.09E-6mol	5.27mL	6.59E-6mol	2.87mL	3.59E-6mol

$$\Phi = \frac{Before_{(moles)} - After_{(moles)}}{X}$$

$$\mathbf{295-350\ nm} \quad 0.57 = \frac{6.7 \times 10^{-6}\ mol - 3.09 \times 10^{-6}\ mol}{x}; x = 4.91 \times 10^{-6}\ Einstein / hour$$

$$\mathbf{>400\ nm} \quad 0.57 = \frac{6.7 \times 10^{-6}\ mol - 6.59 \times 10^{-6}\ mol}{x}; x = 1.93 \times 10^{-7}\ Einstein / hour$$

$$\mathbf{>450\ nm} \quad 0.57 = \frac{6.7 \times 10^{-6}\ mol - 3.59 \times 10^{-6}\ mol}{x}; x = 5.46 \times 10^{-6}\ Einstein / hour$$



## Conclusions

ZnS – Nanoparticles are effective photocatalysts for defluorination of aromatic compounds

No degradation observed in 24 h using Bulk ZnS

Rate of defluorination is related to electron withdrawing or donating ability of substituent



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