Molecularly Tailored Coatings via Variable Duty Cycle Pulsed Plasma Polymerizations: Biomaterials Applications

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Attractive features of plasma polymer films

- Conformal
- Good film thickness control
- Pin hole free
- Singe step, all-dry process

- What about film chemistry control?

Plasma Variables and Film Chemistry

- Nature of the monomer
- Power input
- Flow rate
- Pressure
- Substrate location
- Substrate temperature

Our Approach

Variable duty cycle pulsed plasmas

PULSED PLASMA POLYMERIZATION

VARY RATIO OF PLASMA "ON" TO "OFF" TIMES

SEQUENTIAL CHANGE IN PLASMA DUTY CYCLE

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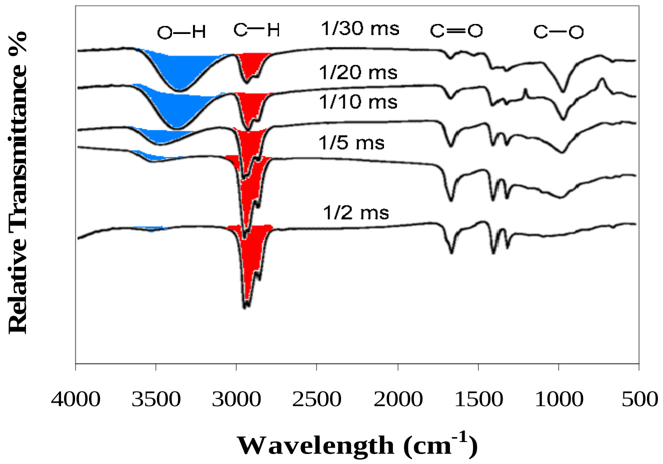
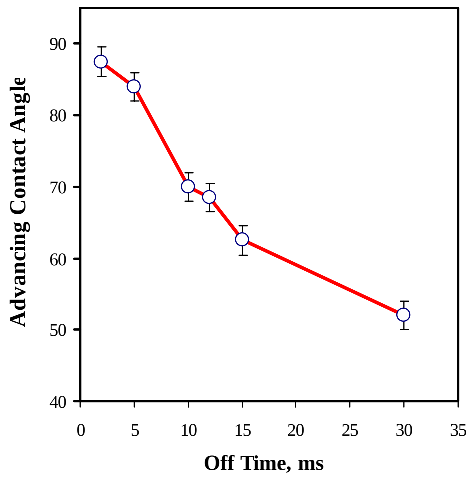
LARGE SCALE PROGRESSIVE CHANGE IN FILM CONDITION

(All other plasma variables held constant)

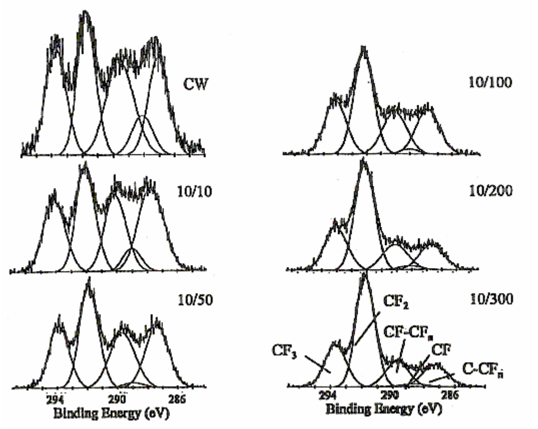
Poly-Allyl Alcohol Films as a Function of Plasma Duty Cycle
Peak Power = 300W



Poly-Allyl Alcohol Films
Increasing Surface Wettability with Increasing Off Time
Plasma On Time = 10ms; Peak Power = 300W



C(1s) XPS of C_6F_{14} Deposited as a Function of Plasma Duty Cycles (peak power 200W)



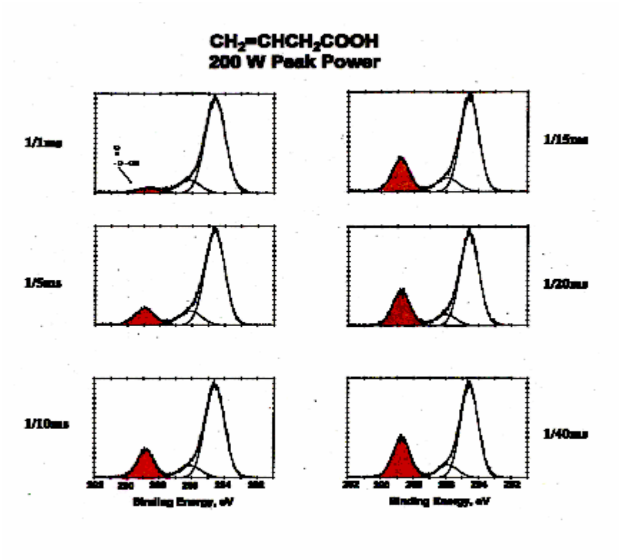
Comparison of Pulsed and CW Depositions under Equivalent Wattage Conditions

$$\text{Equivalent Wattage (Pulsed)} = \frac{\textbf{Plasma ON Time}}{\textbf{Plasma (ON+OFF) Time}} \times \textbf{Peak Power}$$

e.g. 10ms and 50ms off at 300 W
corresponds to
(10/60) x 300W = 50W

e.g. 10μs and 100μs off at 25 W
corresponds to
(10/110) x 25W ≈ 2.25W

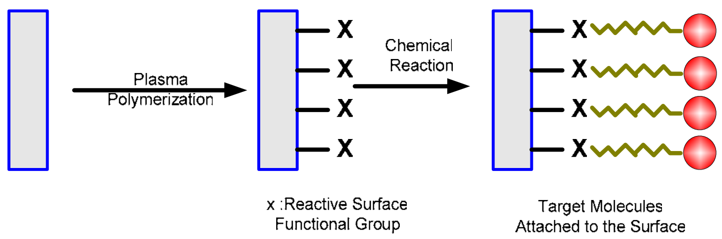
C(1s) XPS of films produced from vinyl acetic acid as a function of plasma duty cycle



Molecular Tailoring of Surfaces

1st Step : Plasma polymerization to introduce reactive surface groups

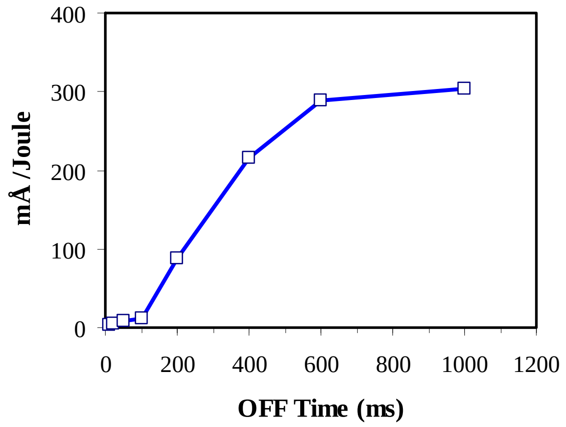
2nd Step : Chemical derivatization to attach target molecules covalently bound to the surface



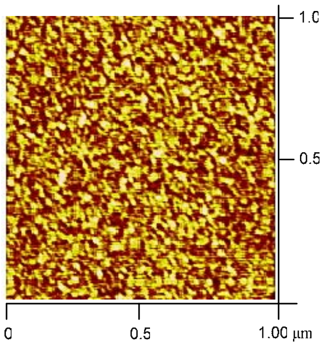
Some Physical Aspects of Films Produced under Pulsed Conditions

- Uniformity
- Roughness
- Stability
- Adhesion and Abrasion Resistance
- Deposition Rates

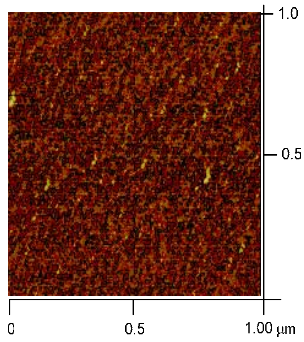
Perfluoropropylene Oxide Monomer
Increasing Energy Efficiency with Increasing Plasma Off-times
and Constant On-time of 10ms
Peak Power = 300W



AFM pictures of plasma polymerized EO2 films



CW 100W, $D_{polymer}$ 25nm, RMS Roughness 0.545



5/115 (P_{eq} 4.3W), $D_{polymer}$ 26nm, RMS Roughness 0.134

Pulsed versus CW Operation

- Film formation under plasma off conditions in pulsed mode
  No substrate bias during plasma off time;
  No short wavelength UV film damage during off times;
  Generally low substrate temperatures.
  Smoother films under pulsed conditions

Drawbacks: Oligomer entrapment in the films
Some loss of film thickness when immersed in solution

Overview of recent plasma studies at UTA

Emphasis has been on development of pulsed plasmas to control film chemistry

Applications

- Electronic Materials
- Biomaterials and Bioanalytical Studies
- Nanoparticles and Nanocomposites

Examples from our Laboratory of Plasma Generated Films used in Biomaterial Applications

- **Non-Fouling Surfaces**
- **Molecularly Structured Affinity Capture Surfaces**
- **Controlled Drug Release**

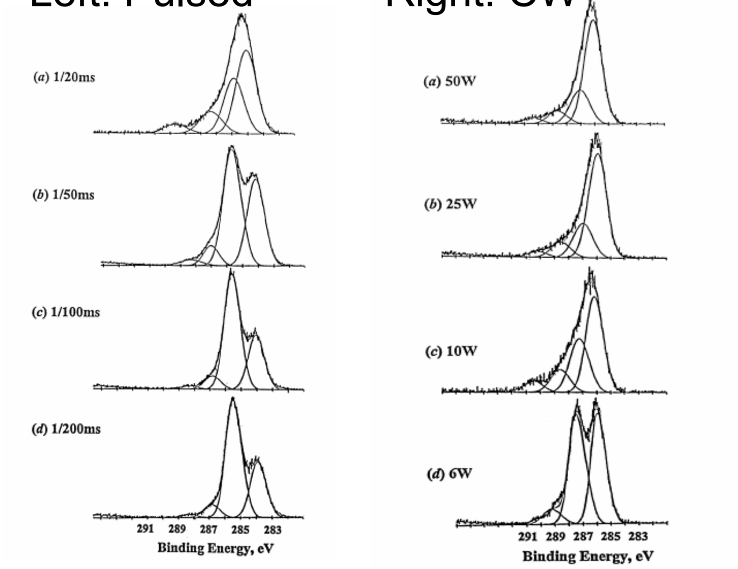
Non-Fouling Surfaces

- Surfaces containing polyethylene oxide units

- -- $(CH_2CH_2O)_n$--

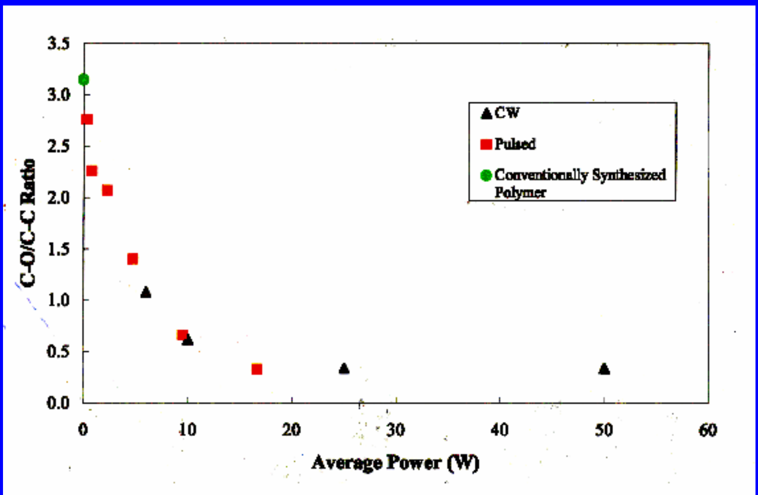
C(1s) XPS of $CH_2{=}CH(OCH_2CH_2)_2OH$

Left: Pulsed Right: CW

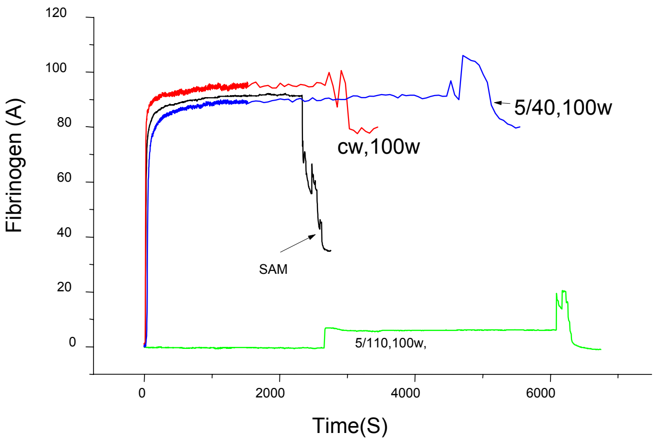


EO2V: Di(ethylene glycol) vinyl ether
$CH_2=CH(OCH_2CH_2)_2OH$

Film Compositional Changes at Ultra Low Power Inputs

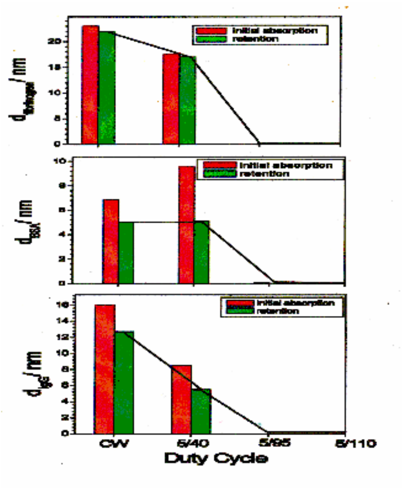


SPR of Fibrinogen Adsorption on Plasma Modified Surfaces



Effect of duty cycle on the absorption

Constant plasma polymer film thickness of d = 25 ±2 nm and constant input power of 100W

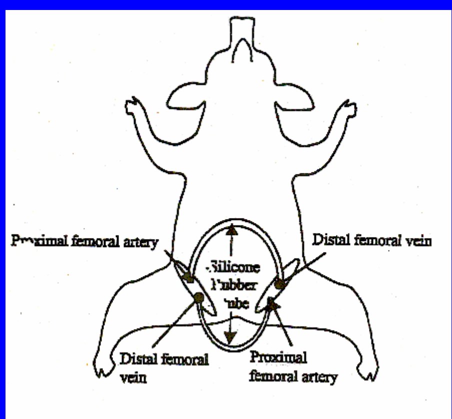


a Fibrinogen

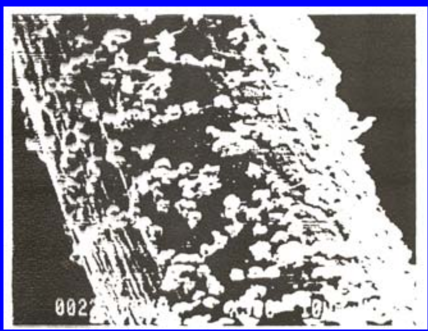
b BSA

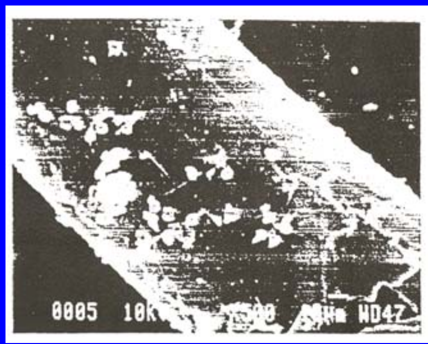
c Immunoglobulin

In-Vivo Experiments



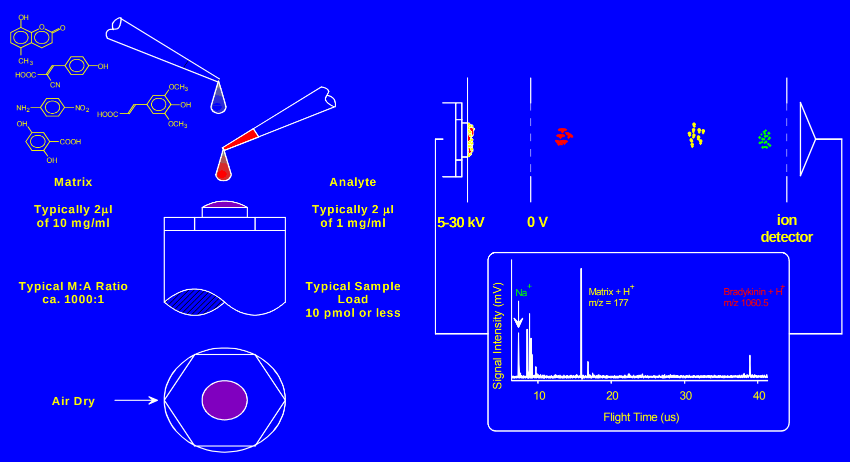
Blood Platelet Adhesion without (left) and with (right) EO2V coating





Plasma Synthesized Bio-Selective Surfaces for use in Proteomics and other Diagnostic Studies using MALDI-MS

Conventional MALDI MS

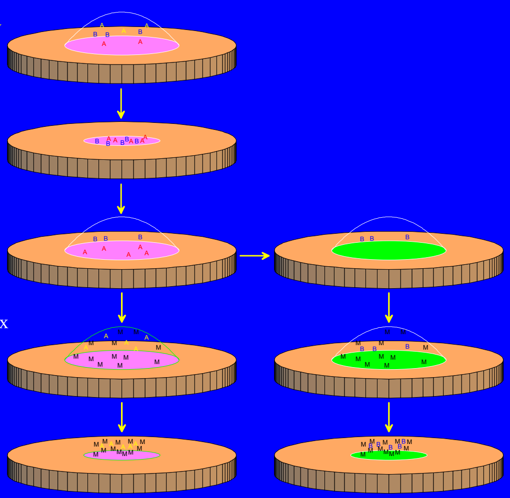


Advantages of MALDI MS

- Relatively Inexpensive (Instruments < $80k are available)
- Simple and Fast (Sample preparation requires mixing 2 solutions and speed is mostly dependent on getting the sample into the mass spectrometer)
- Excellent Performance Parameters (limits of detection in the sub-femtomolar range)
- Easily Automated and Integrated (Compatible with high-throughput robotics)

MALDI MS Based On-Probe Affinity Capture (OPAC) Approaches

1. Deposit mixture of analytes on affinity capture surface.
2. Allow solvents to dry.
3. Add solvent that selectively elutes analyte fraction
4. Add MALDI matrix in solvent that disrupts analyte surface binding.
5. Acquire MALDI mass spectrum of analyte fraction.



6. Deposit eluted analyte fraction on non-fouling surface
7. Add MALDI matrix in solvent that disrupts analyte surface binding.
8. Acquire MALDI mass spectrum of analyte fraction.

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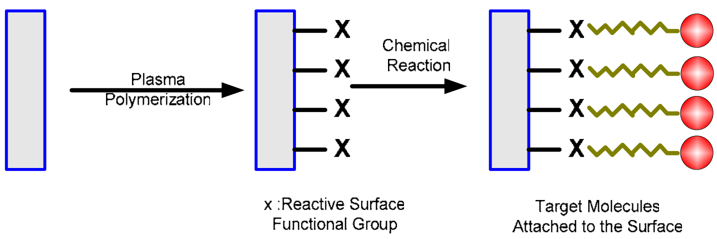
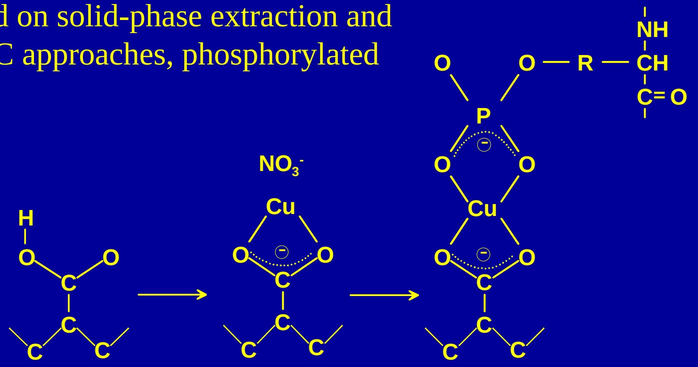
2nd Step : Chemical derivatization to attach target molecules covalently bound to the surface



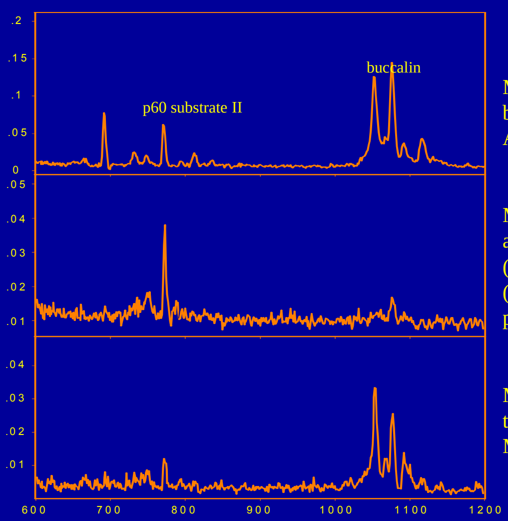
OPAC MALDI MS of Phosphopeptides

Based on solid-phase extraction and IMAC approaches, phosphorylated



compounds are affinity bound to surface immobilized copper salts.

OPAC MALDI MS of Phosphopeptides

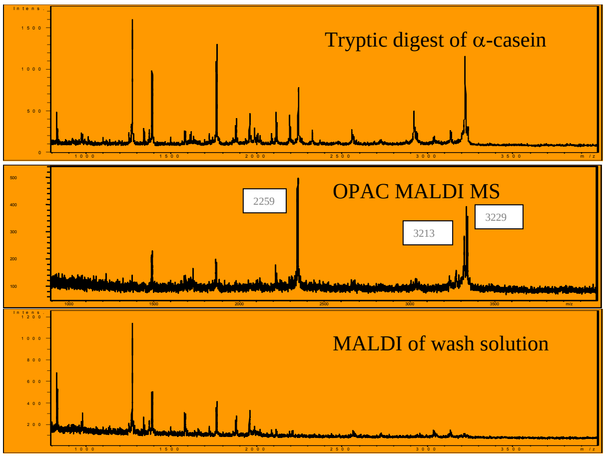


MALDI MS of a mixture of the peptides buccalin and p60 substrate II. (matrix: ACHCA in MeOH).

MALDI MS of the retained peptides after washing the surface with a MES (pH = 5.5) / 10% MeCN buffer. (matrix: ACHCA in MeOH + 0.1 M phosphoric acid).

MALDI MS of the peptides contained in the wash solution. (matrix:ACHCA in MeOH).

OPAC MALDI MS of Phosphopeptides

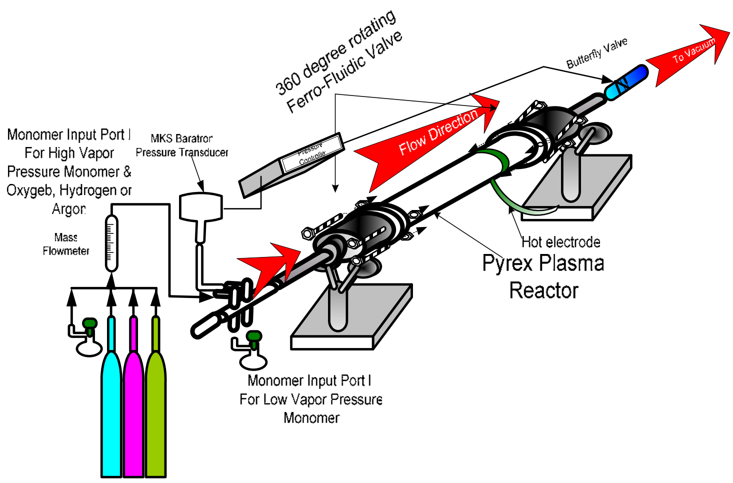


MALDI mass spectra of the tryptic digest peptides of α-casein (matrix: ACHCA).

MALDI mass spectra of retained peptides after washing surface with MeCN/acetic acid/water solution.

Residue	MH^+
121-139	2259
2-29	3213
74-98	3229

360° Rotating Pulsed RF Plasma Reactor



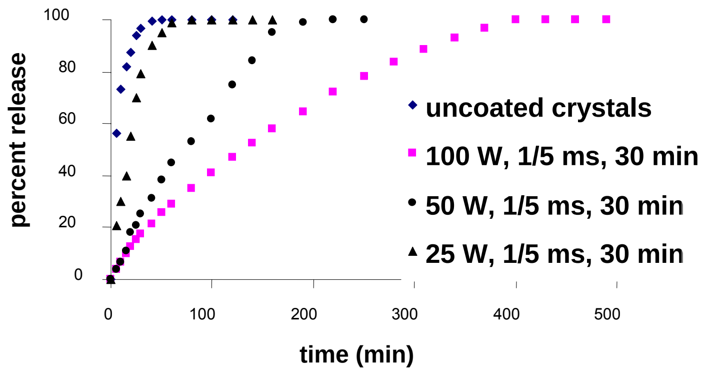
Carboxilic acid modified carbon black

Perfluorohexane Plasma-treated Zeolite Y

Raw zeolite Y

C_6F_{14} plasma treated zeolite Y

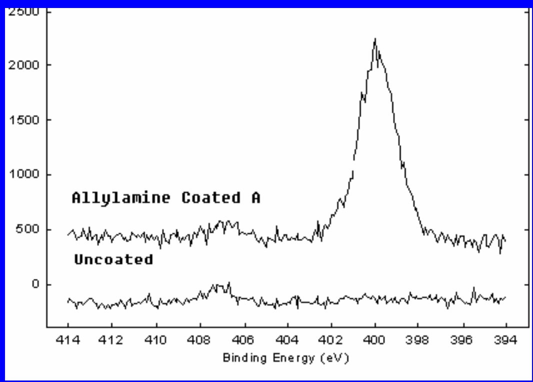
Plasma Coated Aspirin Crystals
Release rates as a function of peak power
Allyl Alcohol Monomer



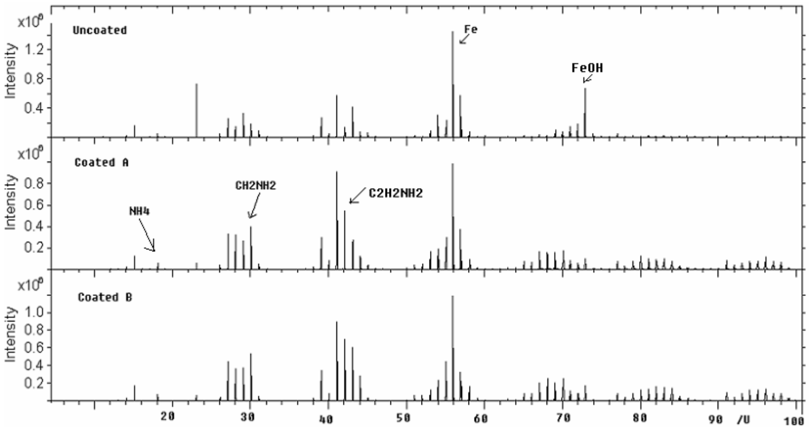
Surface modification of γ- Fe_2O_3 nanoparticles

- For potential applications using the magnetism of these particles in the presence of a magnetic field for focused drug delivery to specifically targeted organs and tissues.

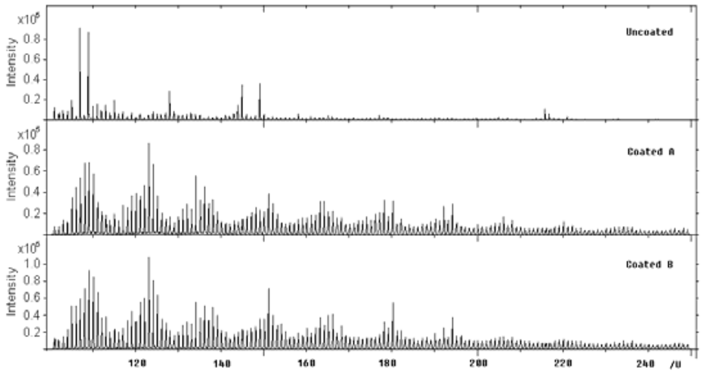
N(1s) XPS of Coated and Uncoated $\gamma - Fe_2O_3$ Nanoparticles



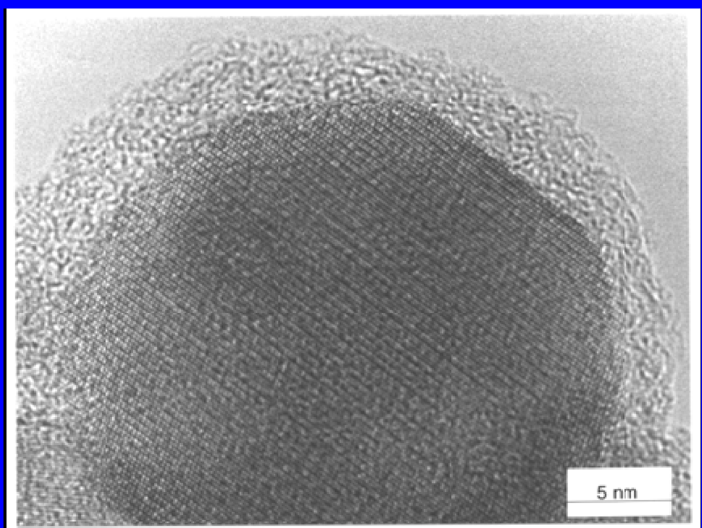
ToF-SIMS of polyallylamine coated Fe_2O_3 nanoparticles



Tof-Sims (continued)



Polyallylamine coated γ – Fe_2O_3



Summation

Plasma technology offers some interesting applications for development of specialized coatings. Although this presentation has emphasized biomaterials, many other application areas are also being investigated in our lab and many other labs around the world.

Co-Workers

- Chuck Savage
- Gary Kinsel
- Jai Cho
- Jing Wu
- Ceren Susut
- Qian Qiu Zhao (DuPont central Research labs)