Environmentally Responsive "Smart" Particles

Presented: IFPRI 2020 Virtual AGM

IFPRI
International Fine Particle Research Institute

Southwest Research Institute

James Oxley, Ph.D.
Staff Scientist
James.Oxley@swri.org
Prepared May 22nd, 2020

Objectives & Scope

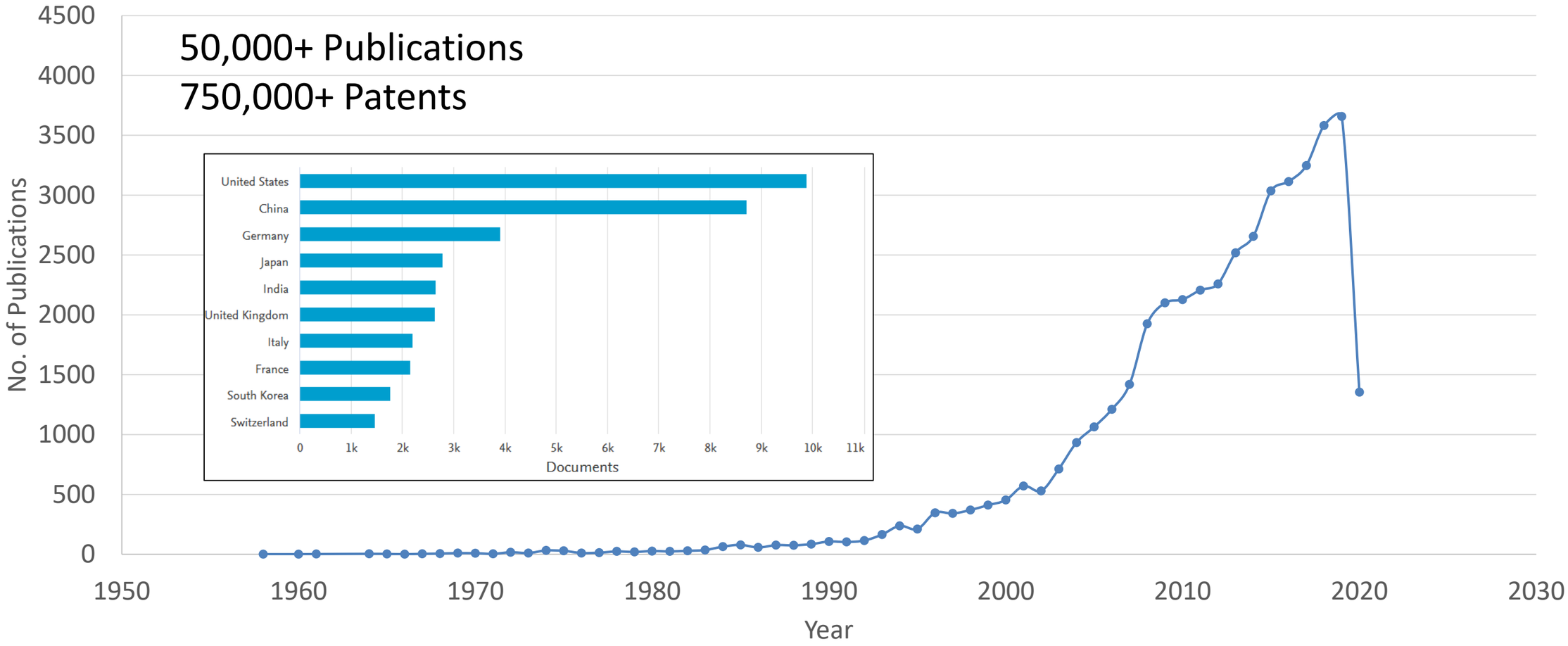
The Search

- Resources:
  - Scopus
  - Google Scholar
  - Patents, Company websites
- Terms:
  - ‘smart particles’, ‘sensor particles’
  - Variations: microspheres, microparticles, environmental, etc.
- Target: academia and industry

The Details

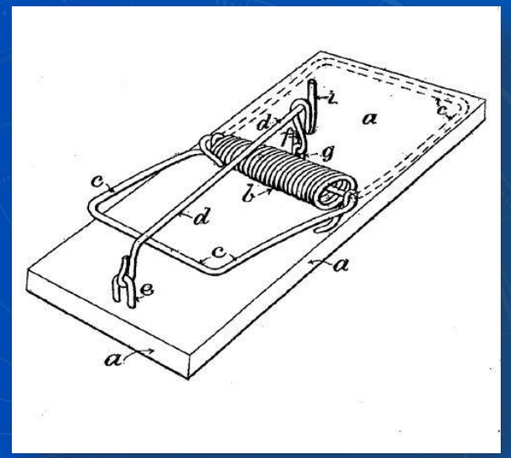
- Operating principles
- Detection
- Analysis
- Control methodologies
- Size range
- Response sensitivity
- Manufacturing

Results

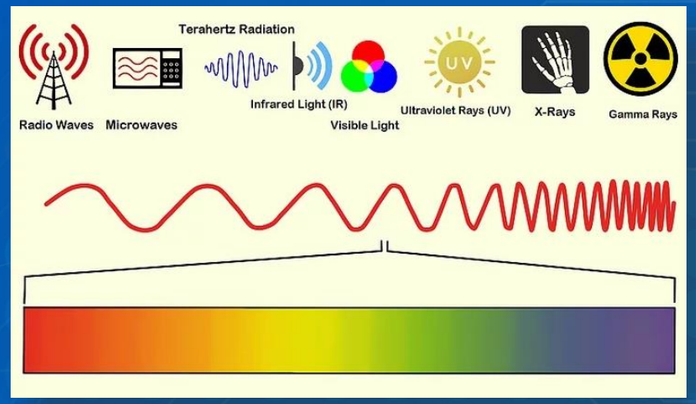


Focusing on publications; filtering based on citation index and keywords.

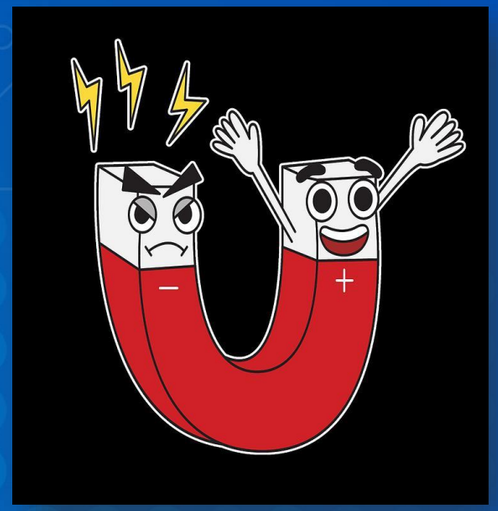
Organization by Trigger/Stimuli



Mechanical



Electromagnetic



Magnetics

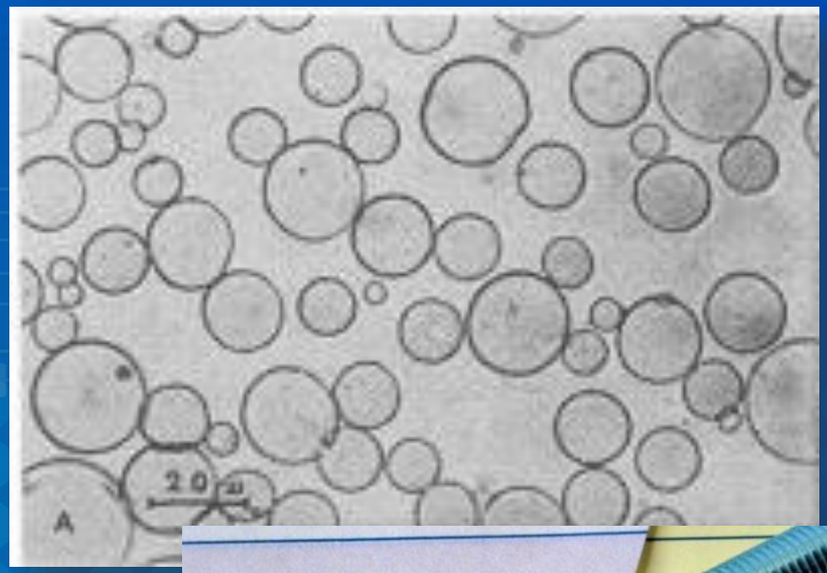
Thermal

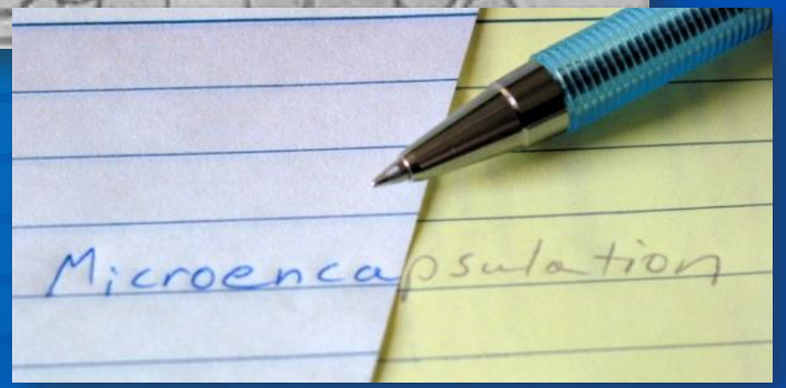
Chemical/pH

Other/Misc

Mechanical

- Applications:
  - Carbonless copy paper
  - Pressure mapping
  - Scratch N' Sniff
  - Adhesives
- Mode of Action
  - Core-shell microcapsules
  - Mechanical fore releases capsule contents
  - Contents: color chemistry, fragrance, adhesives



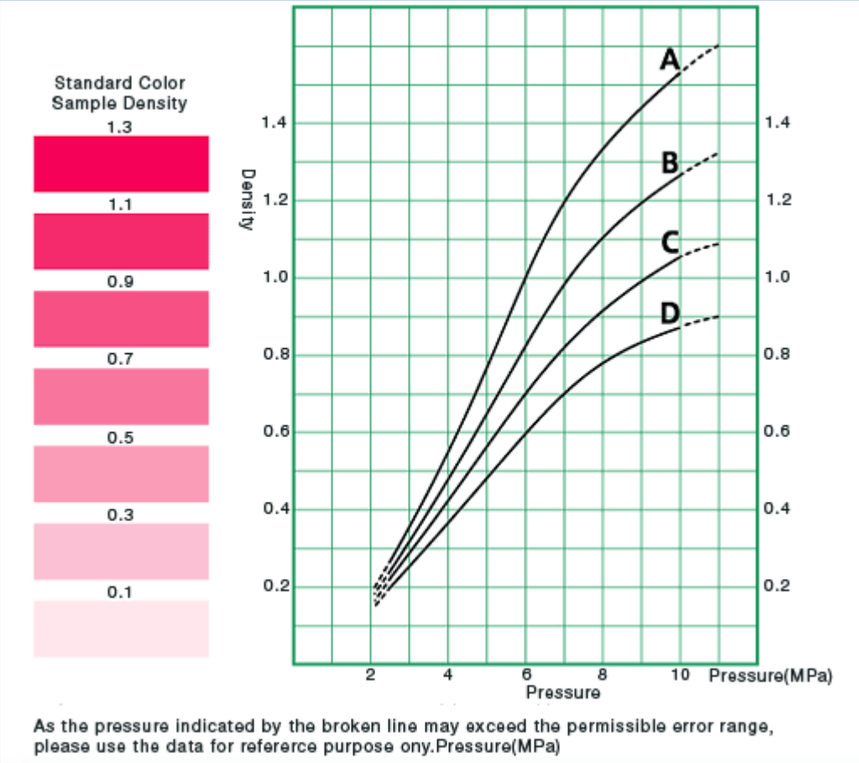


Mechanical Example

- FujiFilm Prescale
- Pressure sensing film applications
- Encapsulated color chemistry activated with microcapsule rupture
- Range: 7.25 to 43,500 psi
- Resolution (spatial): 5-15 µm
- Detection: colorimetric
- Control: color intensity, orientation of developer sheet and capsules
- Manufacturing: interfacial polymerization, polyurea

https://www.fujifilm.com/products/prescale/prescalefilm/

Mechanical Example, cont.



Gasket/seal

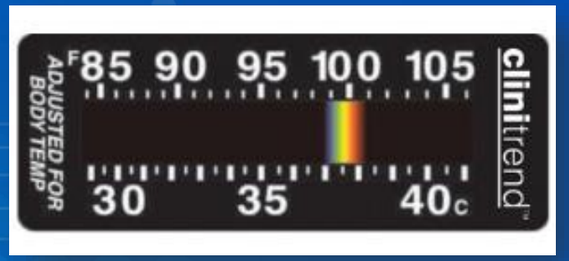
Pressure Film Type	Code	Alternative Code	Pressure Range
Ultra Extreme Low	5LW	UXL310	0.87 - 7.3 PSI (0.06 - 0.51 kg/cm^2)
Extreme Low	LLLLW / 4LW	XL310	7.2 - 28 PSI (0.5 - 2 kg/cm^2)
Ultra Low	LLLW	UL270	28 - 85 PSI (2 - 6 kg/cm^2)
Super Low	LLW	SL270	70 - 350 PSI (5 - 25 kg/cm^2)
Low	LW	L270	350 - 1,400 PSI (25 - 100 kg/cm^2)
Medium	MS	M270	1,400 - 7,100 PSI (100 - 500 kg/cm^2)
High	HS	H270	7,100 - 18,500 PSI (500 - 1,300 kg/cm^2)
Super High	HHS	SH270	18,500 - 43,200 PSI (1,300 - 3,000 kg/cm^2)

Physical Specifications	
Operating Temperature	68°F - 95°F (20°C - 35°C) *much higher for brief exposure*
Humidity Range	20% to 90% RH
Gauge (Thickness)	4 - 20 mils
Spatial Resolution	From 5 - 15 microns
Substrate	Polyethylene Terephthalate (PET)
Accuracy	± 10% visual, ± 2% *Utilizing optional optical measurement systems*
Shelf Life	2 Years

https://www.fujifilm.com/products/prescale/prescalefilm/

Thermal

- Applications
  - Energy phase change materials
  - Expancel
  - Display phase change material (e.g. liquid crystals)
- Mode of action
  - Thermal absorption
  - Triggers phase change
  - Solid → liquid
  - Liquid → gas



Thermal Example

- LCR Hallcrest microcapsules
- Liquid crystal containers
- Phase change activated by heat
- Range: -30 °C to 120 °C
- Precision: +/- 0.1 °C
- Accuracy: +/- 1 °C
- Detection: colorimetric, observation
- Control: liquid crystal chemistry
- Manufacturing: complex coacervation with gelatin/gum acacia shell

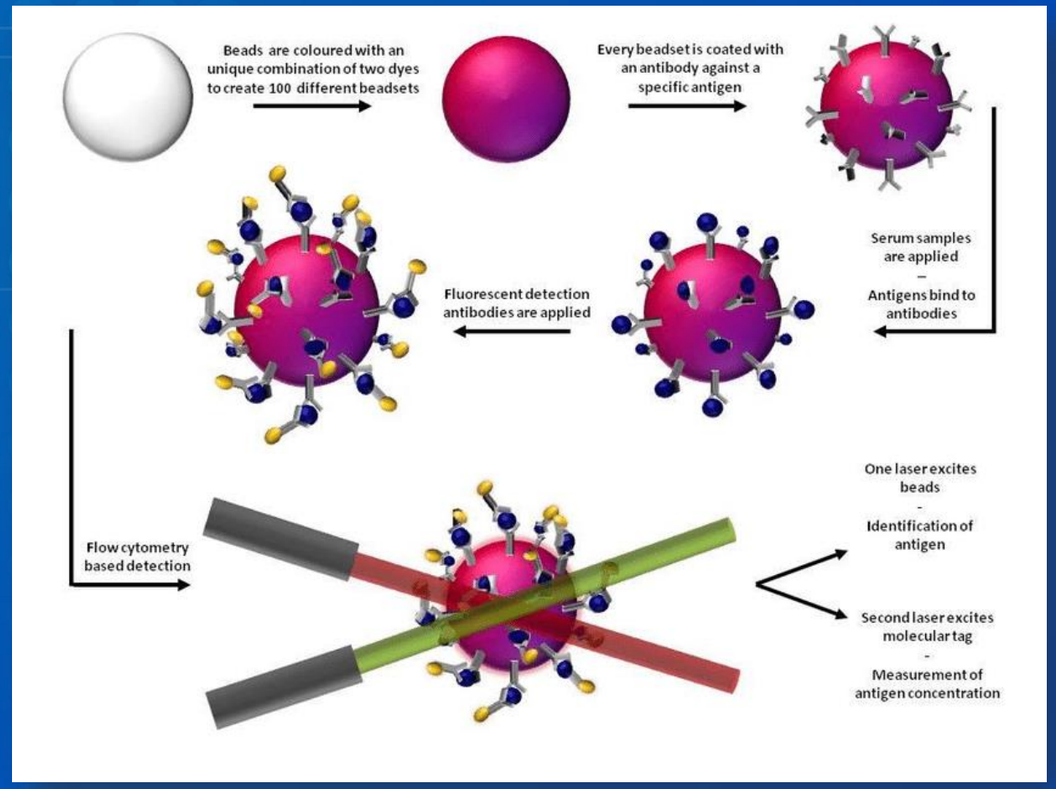
https://www.lcrhallcrest.com/

Chemical/pH

- Applications:
  - Gases
  - Ions
  - Chemical-specific sensor
- Mode of Action
  - Surface-modified particles
    - Higher surface area
    - Better suspension stability, solution homogeneity
  - Disruption/alteration of surface-bound functional groups
    - Change in optical properties (e.g. fluorescence)
    - Change in electrical properties

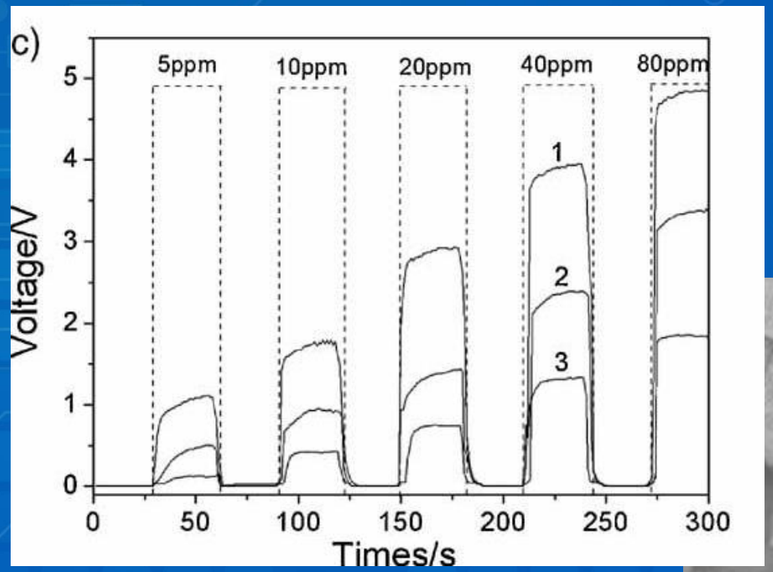
Chemical Example

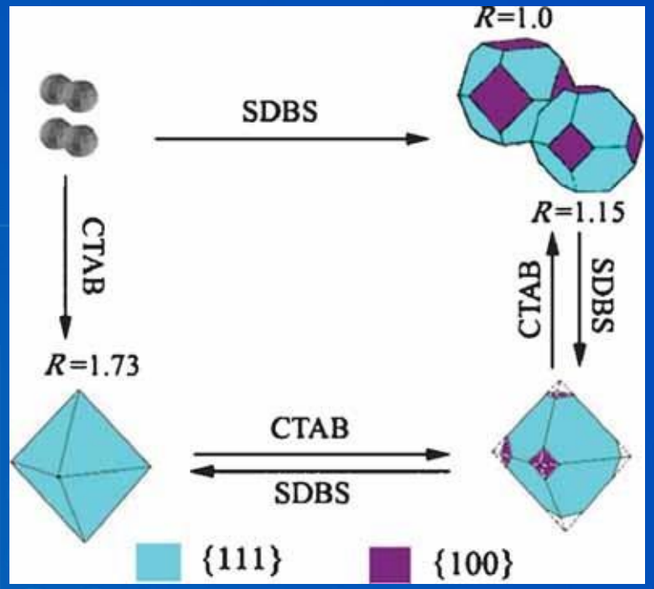
- Luminex xMAP
- Detection and quantitation of proteins, genes, etc.
- Multiple products:
  - MagPlex
  - MagPlex-TAG
  - MicroPlex
  - MagPlex-Avidin
  - SeroMAP
- Particles: carboxylated polystyrene
- Size: 5-6 µm
- Variety: >100 unique spectral signatures
- Manufacturing: Dyeing and surface functionalization of polystyrene beads

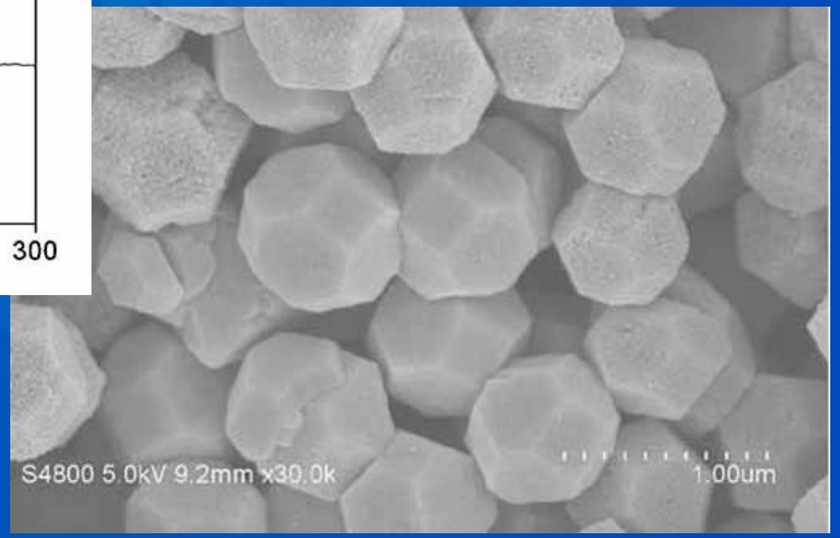


Chemical Example, cont.

- Gas detection (H_2S, formaldehyde, EtOH)
- $ZnSnO_3$ particles
- Size: ~500 nm
- Variations for sensitivity
  - 14-facted polyhedron[1]
  - Octohedron[2]
- Synthesis:
  - controlled precipitation of $ZnAc_2$ and $SnCl_4$
  - Varied surfactants and NaOH soln.
- Voltage measured across particles deposited on ceramic tube



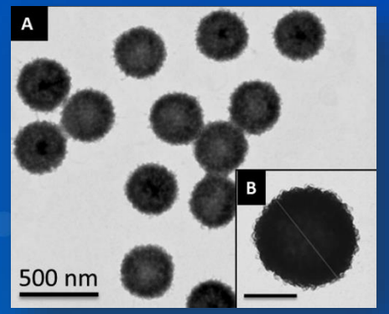


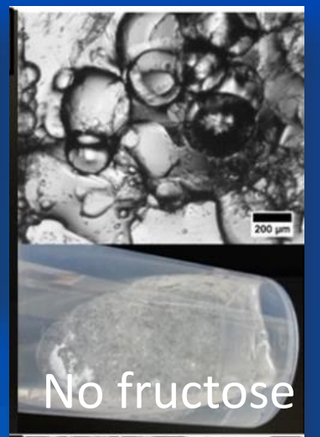


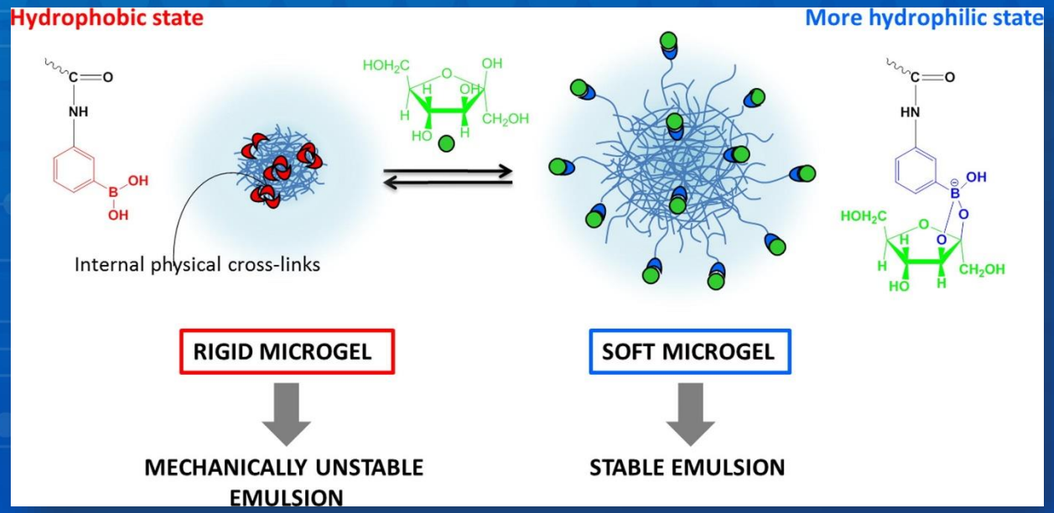
Geng, B.; Fang, C.; Zhan, F.; Yu, N. Synthesis of Polyhedral ZnSnO3 Microcrystals with Controlled Exposed Facets and Their Selective Gas-Sensing Properties. *Small* **2008**, *4* (9), 1337–1343. https://doi.org/10.1002/smll.200701177.

pH Example

- Sugar-Responsive Pickering Emulsion
- Functionalized poly(*N*-isopropylacrylamide) microgel
- Synthesis: aqueous free-radical precipitation polymerization
- Pickering with dodecane as model core oil
- Microgel size: 300-900 nm (soln. dependent)
- Emulsion size: ~200 µm
- Sensitivity: 0-20 mM







Tatry, M.-C.; Qiu, Y.; Lapeyre, V.; Garrigue, P.; Schmitt, V.; Ravaine, V. Sugar-Responsive Pickering Emulsions Mediated by Switching Hydrophobicity in Microgels. *J. Colloid Interface Sci.* **2019**, *561*, 481–493. https://doi.org/10.1016/j.jcis.2019.11.023.

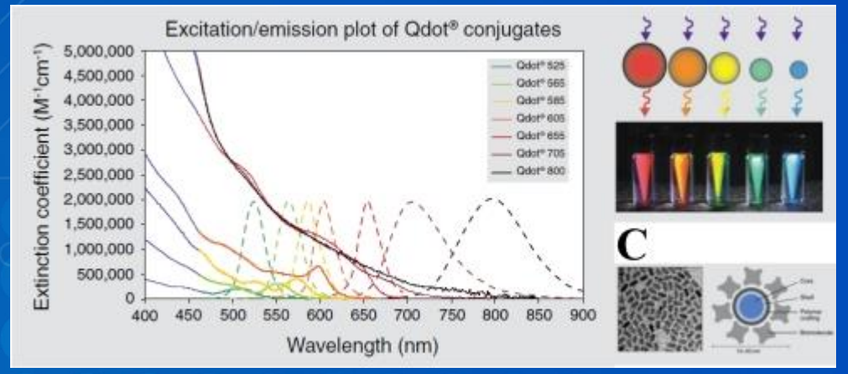
Electromagnetic Radiation

Applications

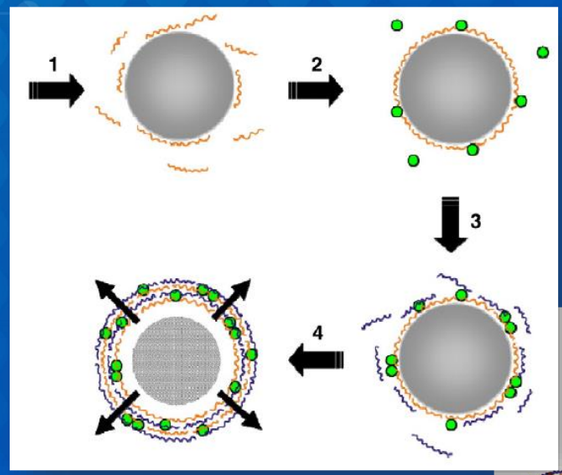
- Near-IR Thermal Therapy
- Quantum Dots
- Photoresponsive release

Mode of Action

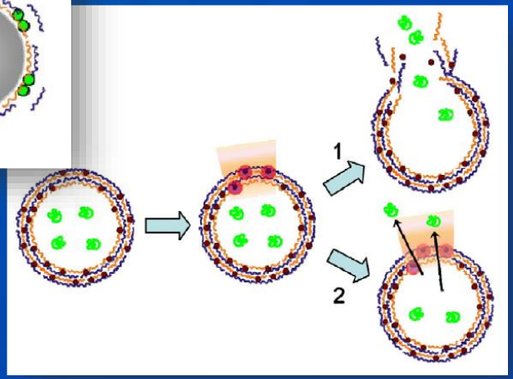
- UV/Visible absorbance → Fluorescence
- IR absorbance → heat
- UV absorbance → degradation



Invitrogen Qdots®

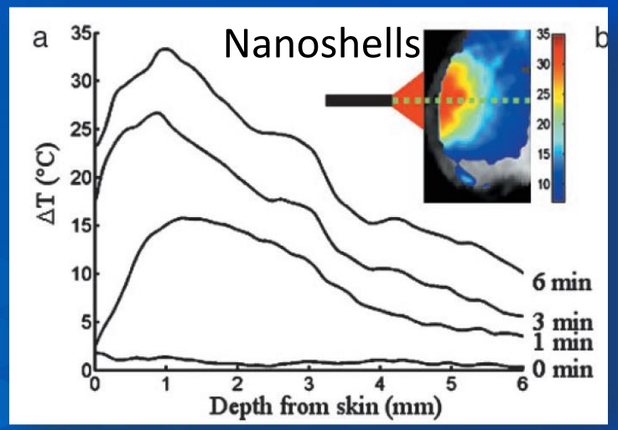


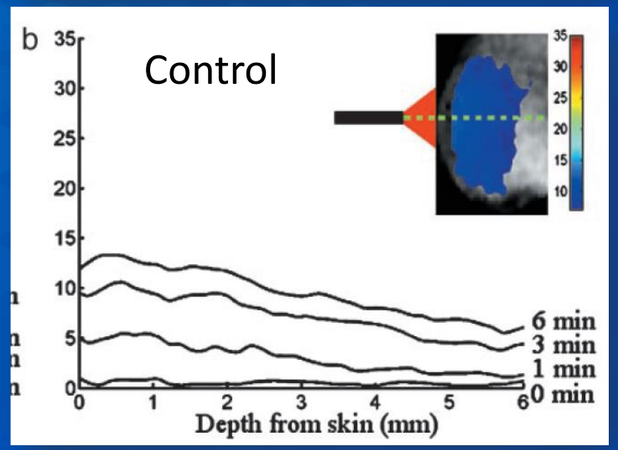
Bédard, 2010



Electromagnetic Radiation Example

- Nanospectra Biosciences
- Technology: AuroLase® tumor ablation
  - Aminated silica particles prepared via Stöber process
  - Colloidal gold adhered to amine surface
  - Shell growth via $HAuCl_4$
  - Functionalized with thiolated PEG
  - IV injection; accumulate in tumor
- Size: 110 ± 11 nm core, 10 nm shell
- 820 nm laser irradiation, irreversible tumor damage





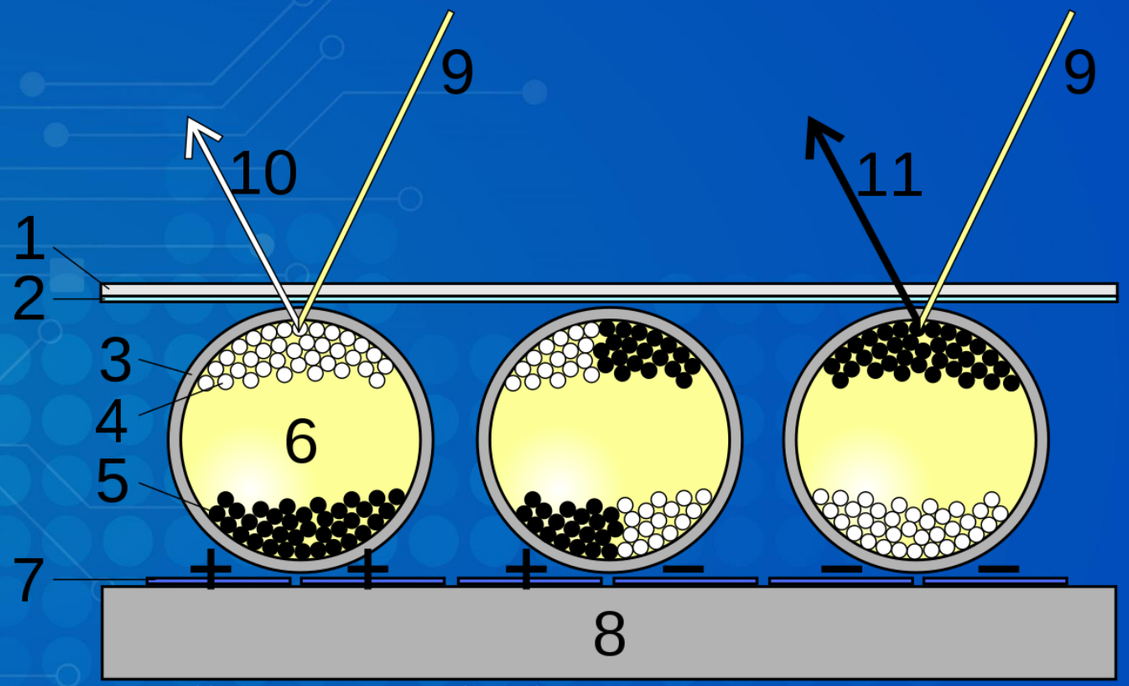
NANOSPECTRA

Hirsch, L. R.; Stafford, R. J.; Bankson, J. A.; Sershen, S. R.; Rivera, B.; Price, R. E.; Hazle, J. D.; Halas, N. J.; West, J. L. Nanoshell-Mediated near-Infrared Thermal Therapy of Tumors under Magnetic Resonance Guidance. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100* (23), 13549–13554. https://doi.org/10.1073/pnas.2232479100.

Magnetic/Electric Fields

Applications

- Electrophoretic displays
- Magnetic particle actuation
- Oil/Water separation
- MRI contrast agents
- Chemical/Biosensors



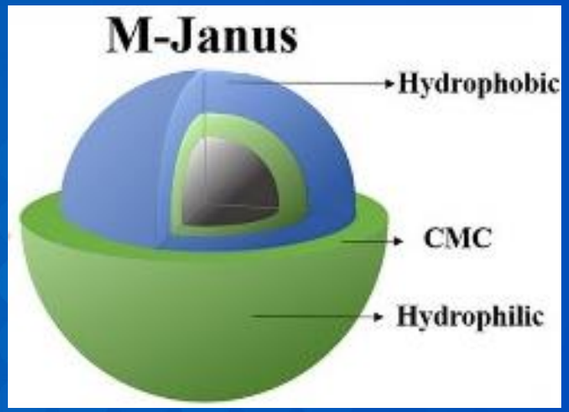
https://en.wikipedia.org/wiki/E_Ink

Mode of Action

- Particles composed of magnetically or electrically sensitive materials
- Oscillation or introduction of field alters particle behavior

Magnetic/Electric Field Example

- Magnetically induced oil/water separation w/ Janus particles
- Technology: Janus iron oxide particles
- Preparation:
  - Iron-Oxide core
  - Carboxymethyl cellulose/ethyl cellulose shell
- Size: ~100 nm
- Saturation magnetism: 69.7 emu/g
- Emulsion displacement via strong hand magnet
- Demonstrated recycling/reuse



He, X.; Liang, C.; Liu, Q.; Xu, Z. Magnetically Responsive Janus Nanoparticles Synthesized Using Cellulosic Materials for Enhanced Phase Separation in Oily Wastewaters and Water-in-Crude Oil Emulsions. *Chem. Eng. J.* **2019**, *378*. https://doi.org/10.1016/j.cej.2019.122045.

Other Systems: Microencapsulation

Applications

- Pharmaceuticals
- Nutraceuticals
- Food
- Cosmetics
- Consumer Products
- Agriculture
- Paints & Coatings
- Other Industrial Applications

Mechanisms

- Mechanical
- Thermal
- pH
- Dissolution
- Diffusion
- Biodegradation
- Osmotic
- No release

Indoor Applications

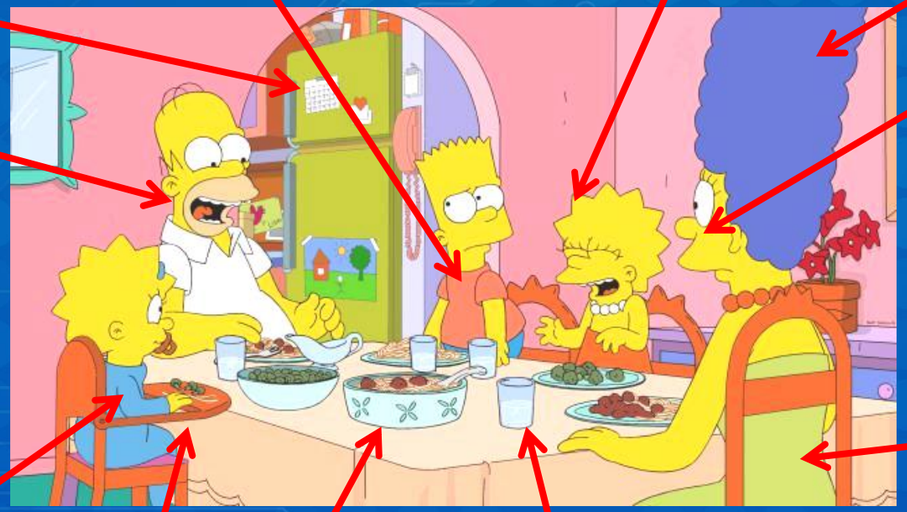
Cleaning products

Deodorant

Fragrances

Hair care

Toothpaste



Cosmetics

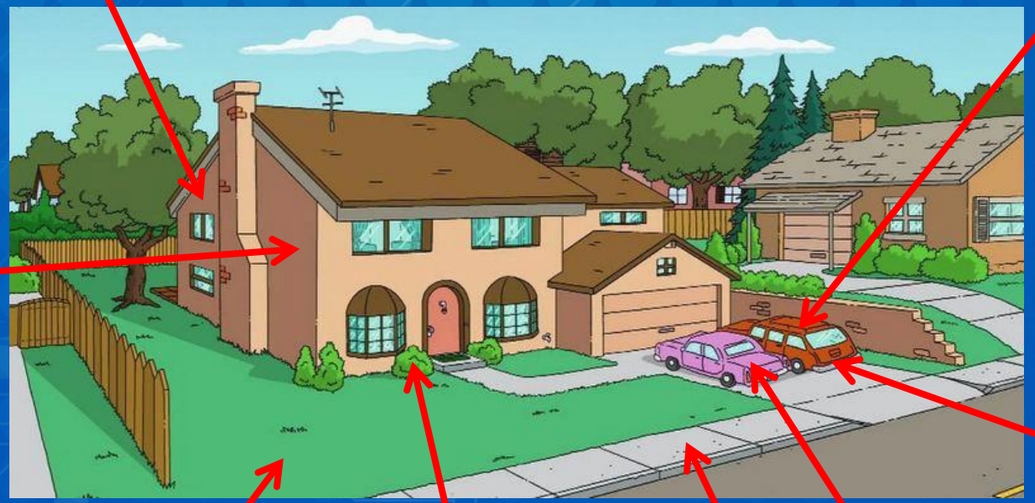
Laundry

Vaccines

Flavors & nutrients

Beverages

Outdoor Applications



Conclusions and Next Steps

Conclusions

- Variety of particles, applications, triggers, and responses
- Mechanical, thermal, chemical, electromagnetic, magnetic, etc.
- Successful commercial examples, and emerging academic solutions

Next Steps

- Collect feedback from IFPRI membership
- Complete written review
- Final goals:
  - Balance of commercial and academic examples
  - Not intended to be a catalog; rather survey of different approaches/applications

Thank You

Independent, Non-Profit Contract R&D
+3000 Employees
2 Million Sq. Ft. Laboratory Space

$600 Million Annual Revenue
Established 1947
San Antonio, TX