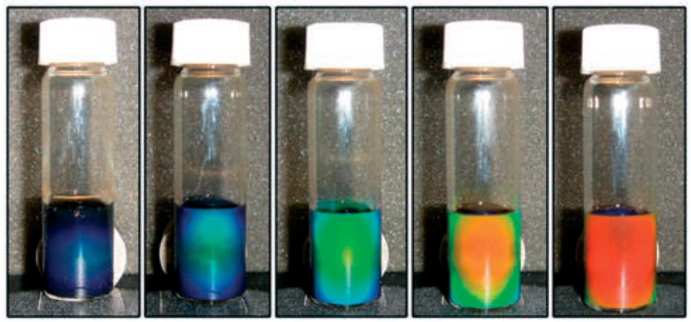
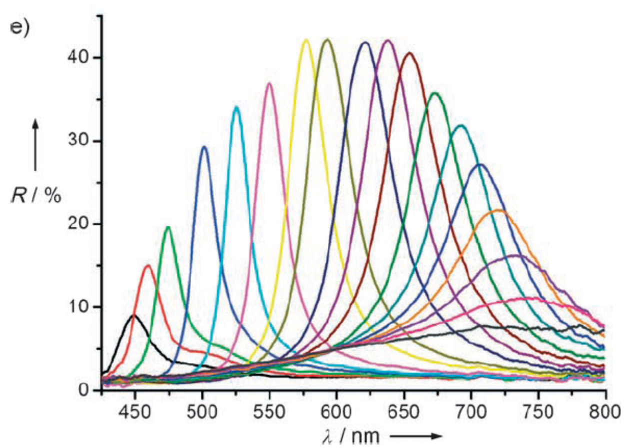
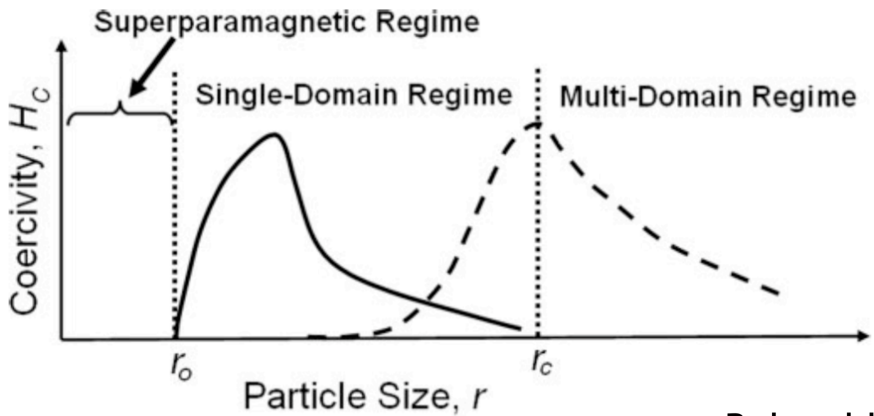
Superparamagnetic nanoparticle arrays for magnetically tunable photonics



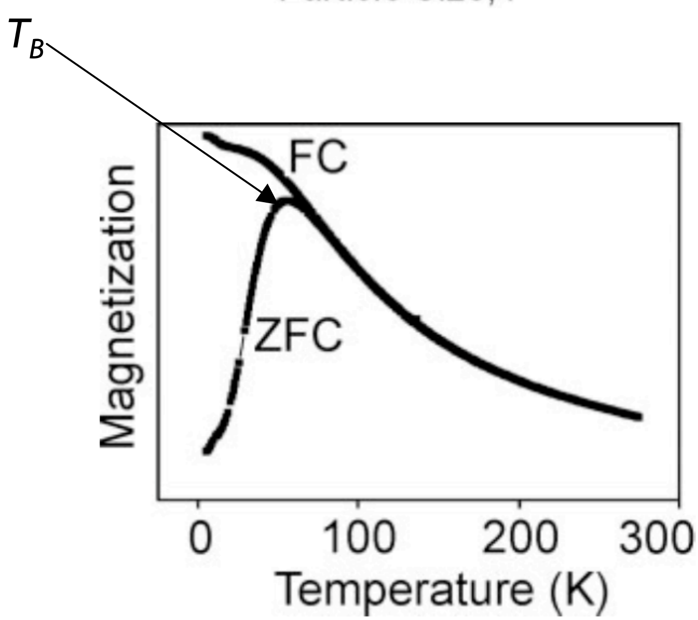
Josh Kurzman
Materials 265



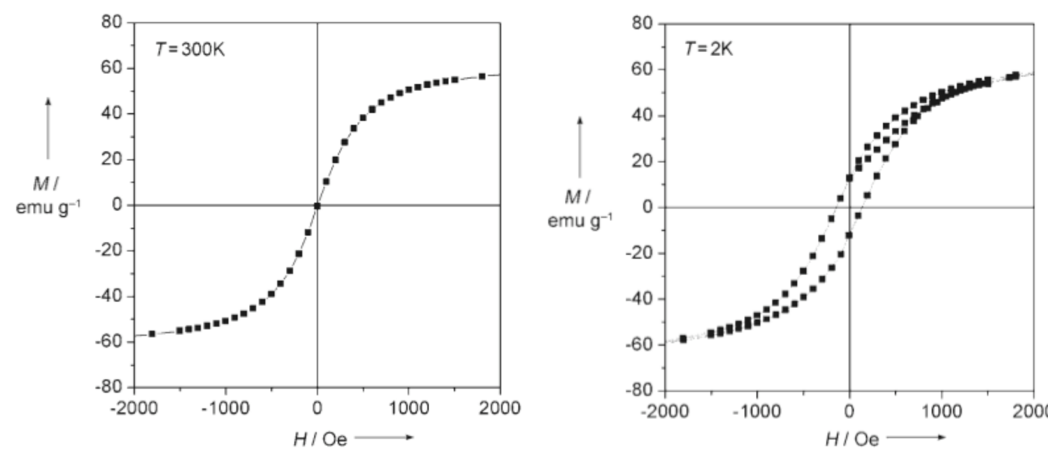
Superparamagnetism



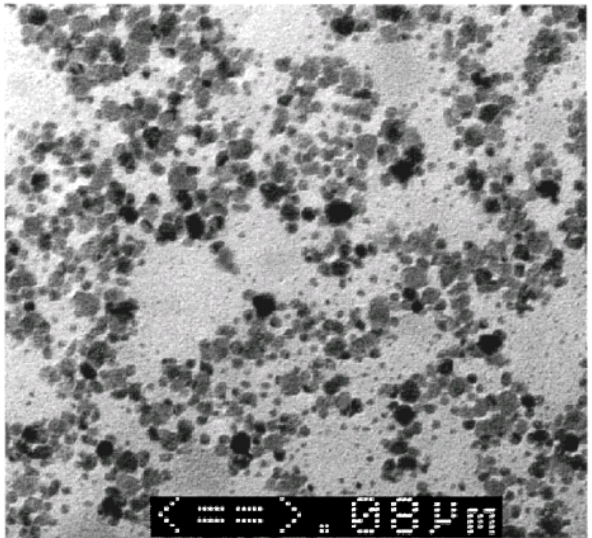
In SPM regime, thermal energy sufficient to overcome spin reversal barrier

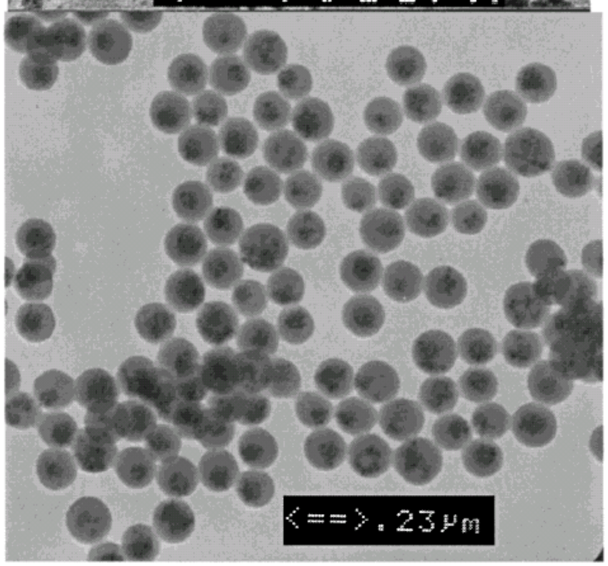


Below blocking temperature, T_B, not enough energy to reverse spins, ---> remenance and coercivity.



Preparations - embedded SPM composites





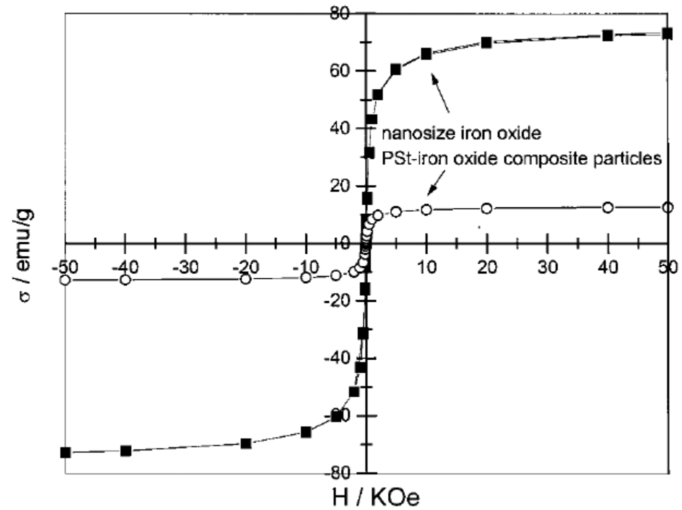
coprecipitation of Fe(II) and Fe(III) chloride with NH_4OH at RT

↓

2-15 nm Fe_2O_3 maghemite (10 nm avg. diameter)

emulsion polymerization ↓

Polystyrene (PSt) - iron oxide composites



No remanence or coercivity at RT

X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, and S. A. Asher, *Chem Mater*. **2002**, *14*, 1249-1256

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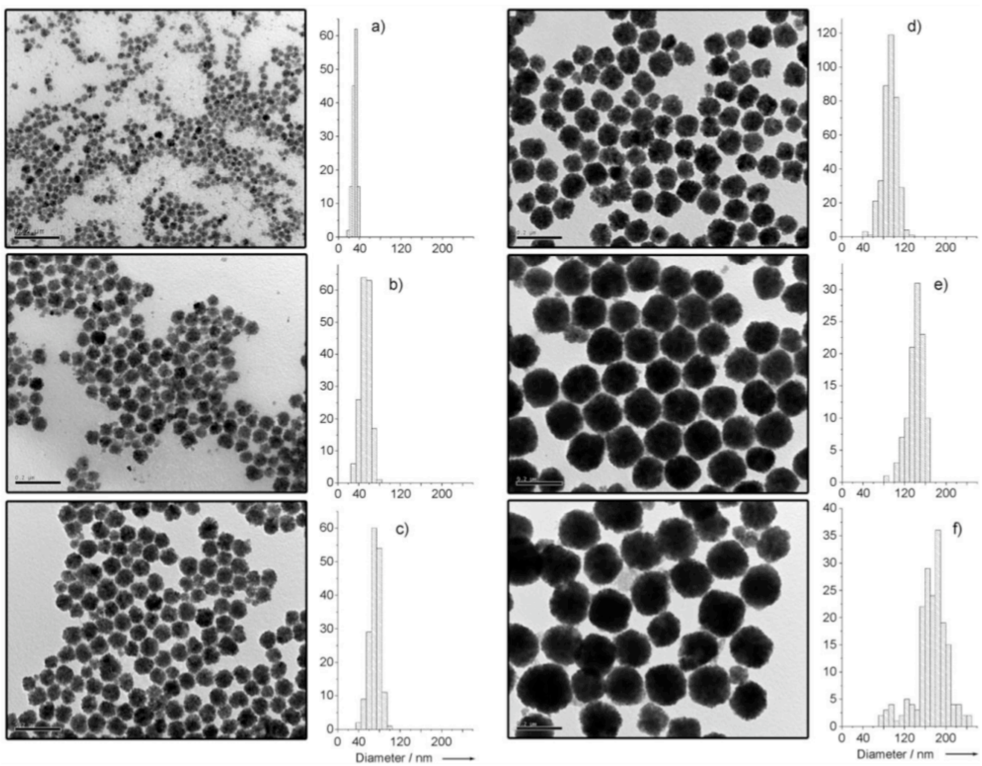
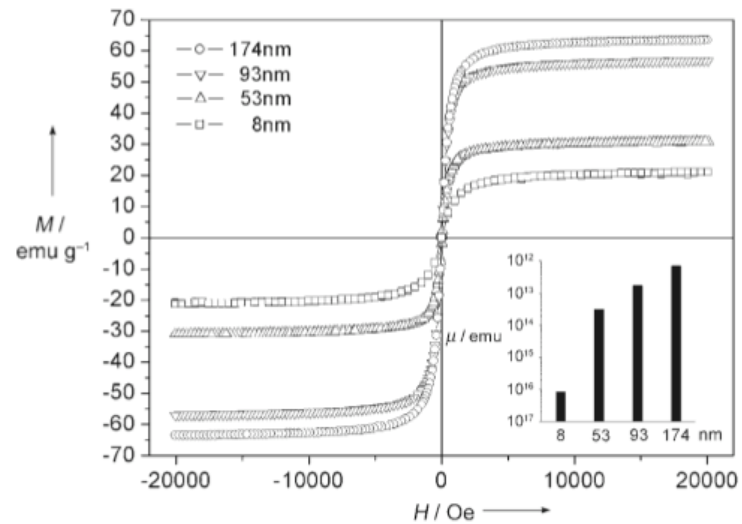
Preparations - Fe_3O_4 size control

Poly acrylic acid (PAA) + $FeCl_3$ in DEG at 220°C
10 : 1

just precipitate with appropriate amount of NaOH



Differences in saturation magnetization likely due to higher weight fraction of PAA in smaller particles



Trend in μ suggests clusters of SPM nanoparticles offer better field response than quantum dot

ex) 10, 10.3, 10.6, 11.2, 11.5 equiv. NaOH

↓

31, 53, 71, 141, and 174 nm (avg. sizes)

J. Ge, Y. Hu, M. Biasini, W. P. Beyermann, and Y. Yin, *Angew. Chem. Int. Ed.* **2007**, *46*, 4342-4345

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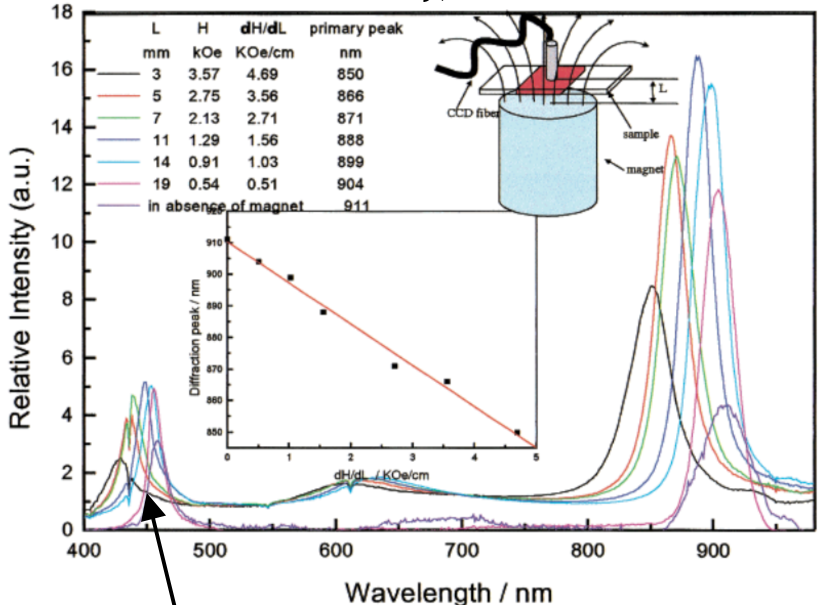
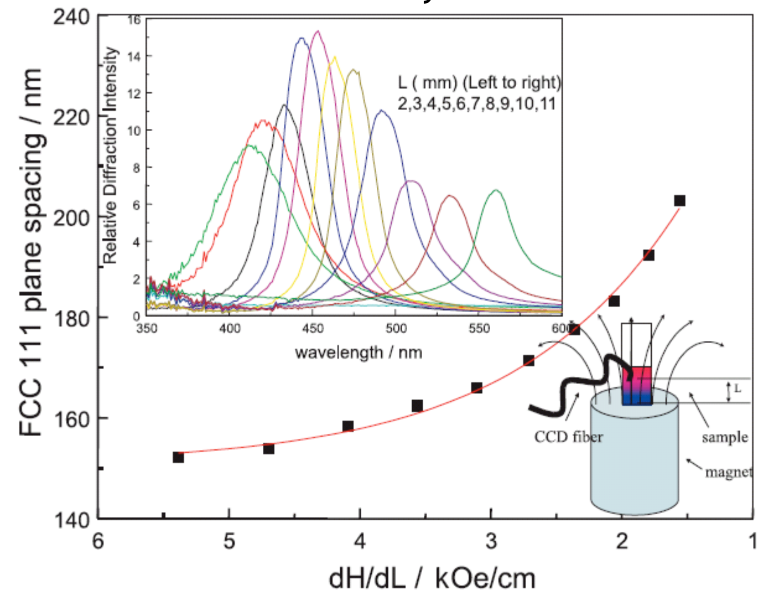
Optical response of PSt-Fe_2O_3 composites

Bragg diffraction of vis/IR radiation modified by varying field strength (magnet to sample distance)

Thin array, 2.5 vol%



Thick array 4.2 vol%



2nd order diffraction

Note the high fields needed to overpower electrostatics

Highly charged surfaces on PSt-Fe_2O_3 composites, strong electrostatics drive ordering in absence of H.

X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, and S. A. Asher, *Chem Mater*. **2002**, *14*, 1249-1256

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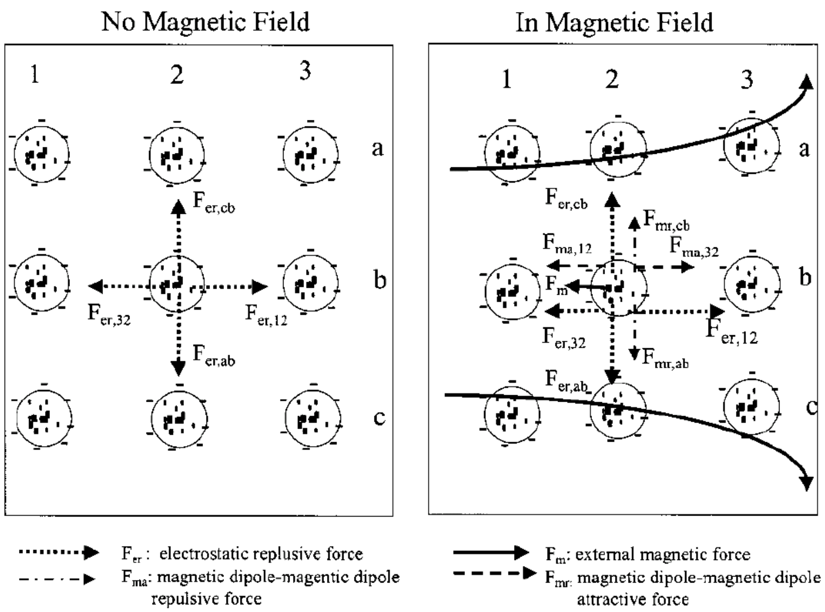
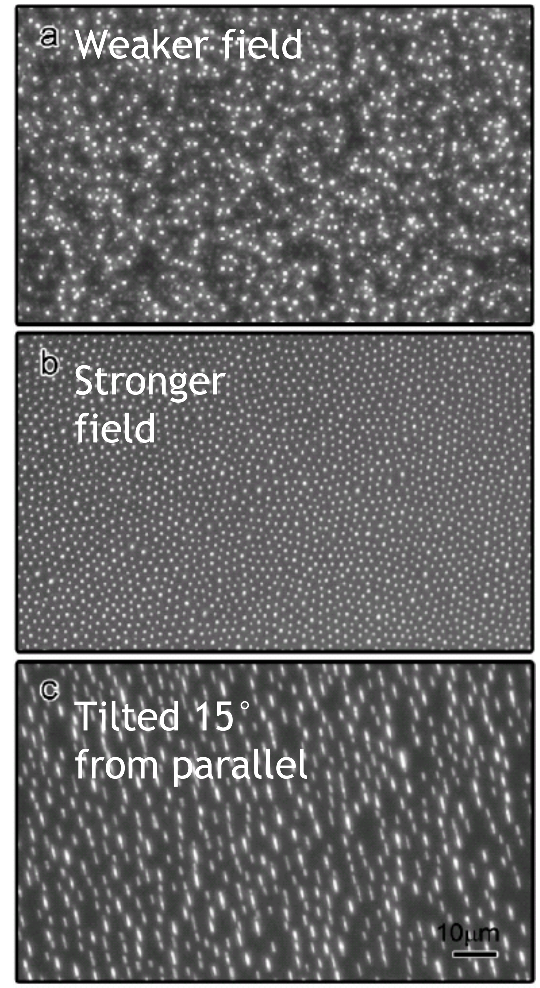
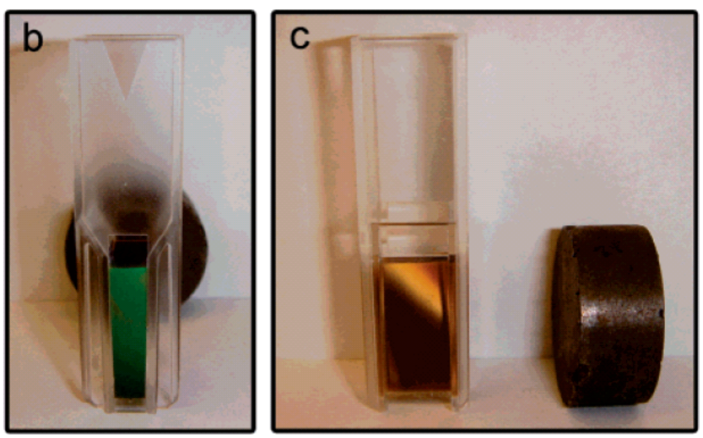
Colloid assembly in a magnetic field



Balance between electrostatic repulsions and magnetic dipole interactions

Particles attracted to maximum of local magnetic field gradient, compressed parallel to field





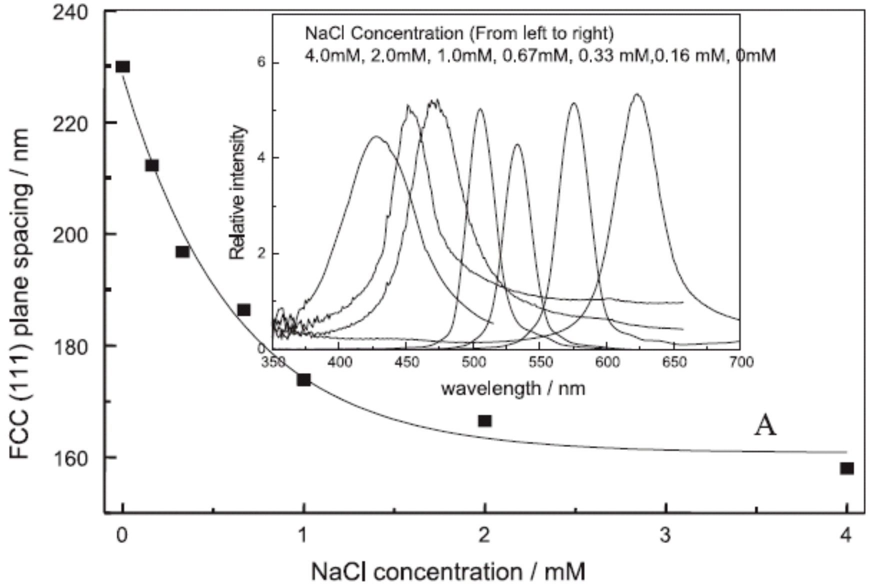
1D chains self assemble parallel to magnetic field

Structural anisotropy leads to anisotropic optical response

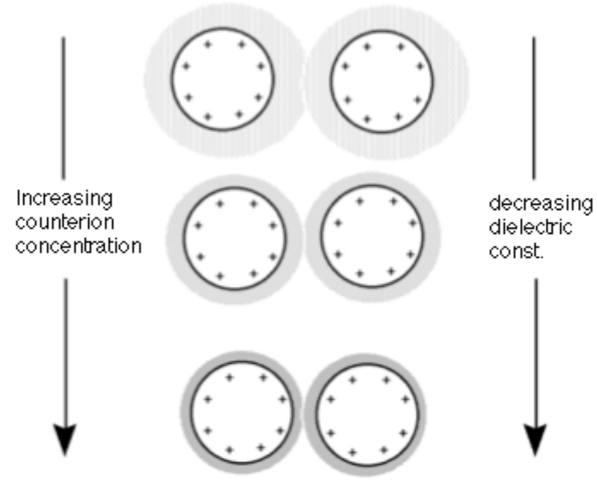
X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, and S. A. Asher, *Chem Mater*. **2002**, *14*, 1249-1256

J. Ge, Y. Hu, T. Zhang, T. Huynh, and Y. Yin, *Langmuir* **2008**, *24*, 3671-3680

Tuning the interparticle potential

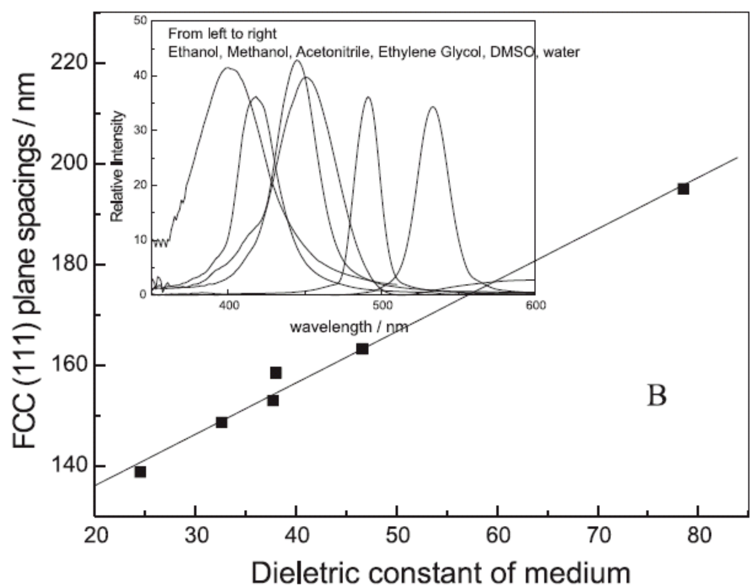


Raising counter ion concentration increases screening



Counter Ion Cloud

Electrostatic Double Layer



Debye length, "thickness" of the double layer, proportional to $\varepsilon^{1/2}$. Decrease in plane spacing with decrease in dielectric constant

higher packing densities
blue shift

X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, and S. A. Asher, *Adv. Mater.* **2001**, *13*, 1681-1684

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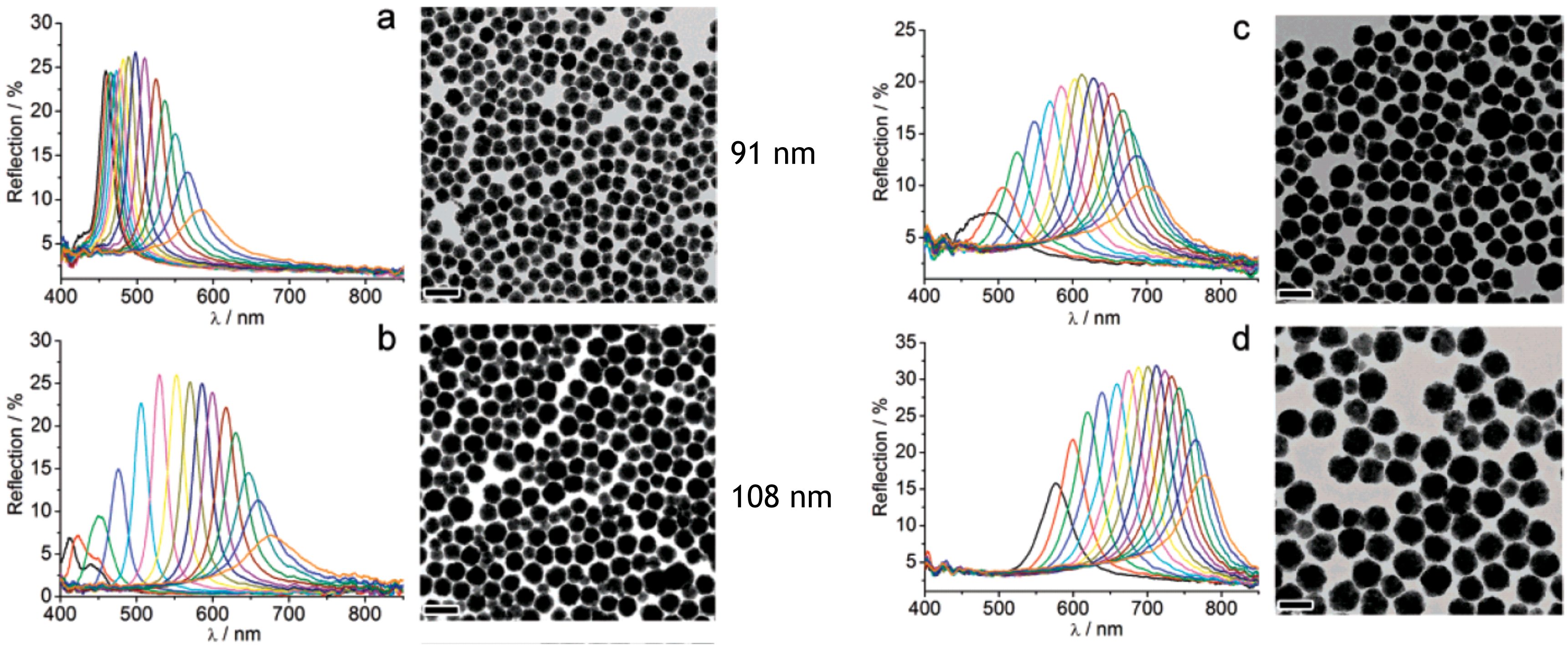
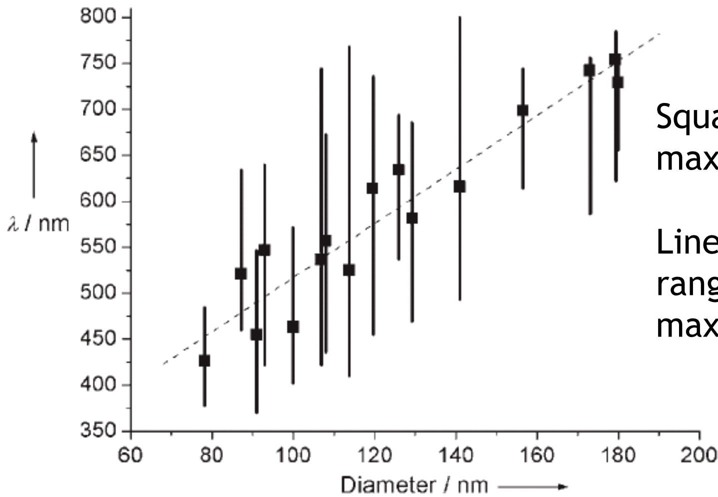
Tuning range and particle size

Scale bars = 200 nm





Squares denote max intensity

Lines indicate range ≥ 30% max intensity

Larger inter-cluster spacings, red shift

Stronger fields needed for smaller clusters, larger clusters order in weaker fields

Note: fields on order of 100 - 500 G for Fe_3O_4 tuning

J. Ge, Y. Hu, T. Zhang, T. Huynh, and Y. Yin, *Langmuir* **2008**, *24*, 3671-3680

J. Ge, Y. Hu, and Y. Yin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7428-7431

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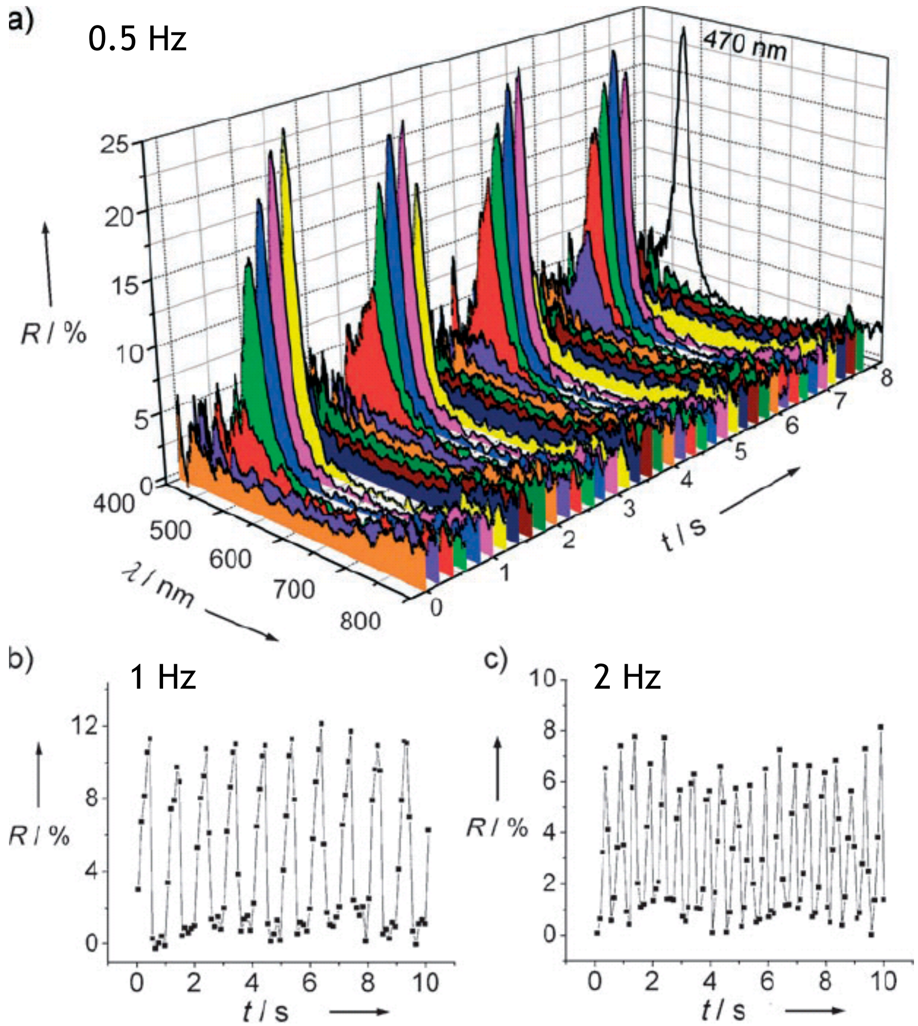
Responsive photonic modulation

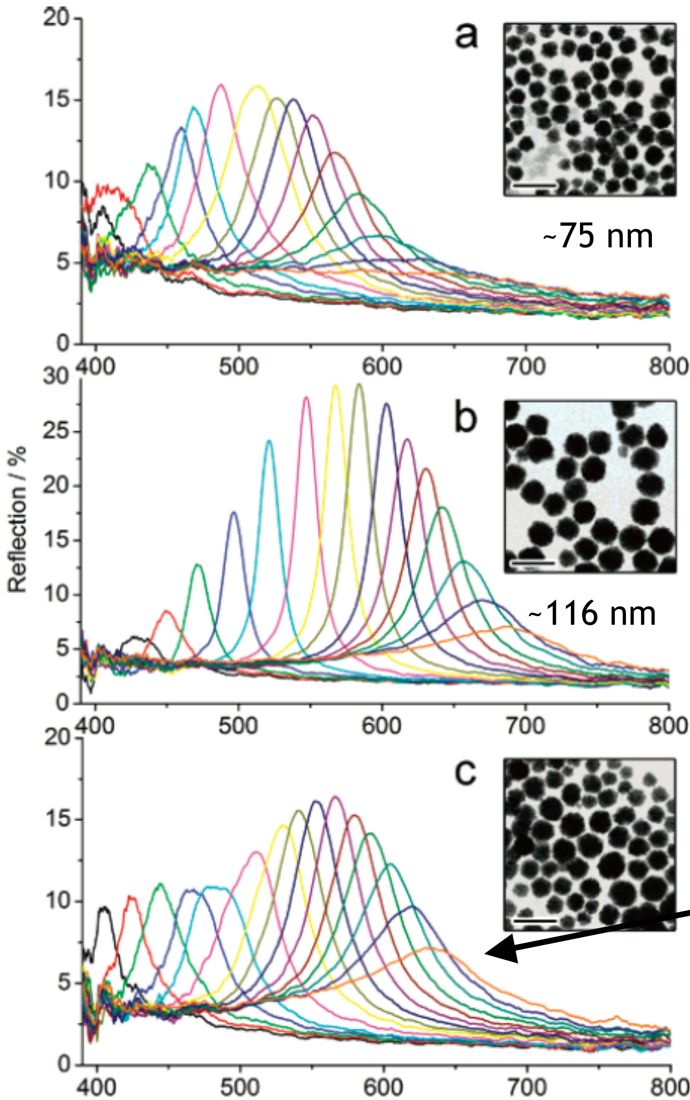
70 nm Fe_3O_4 colloids in a periodic magnetic field



J. Ge, Y. Hu, and Y. Yin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7428-7431

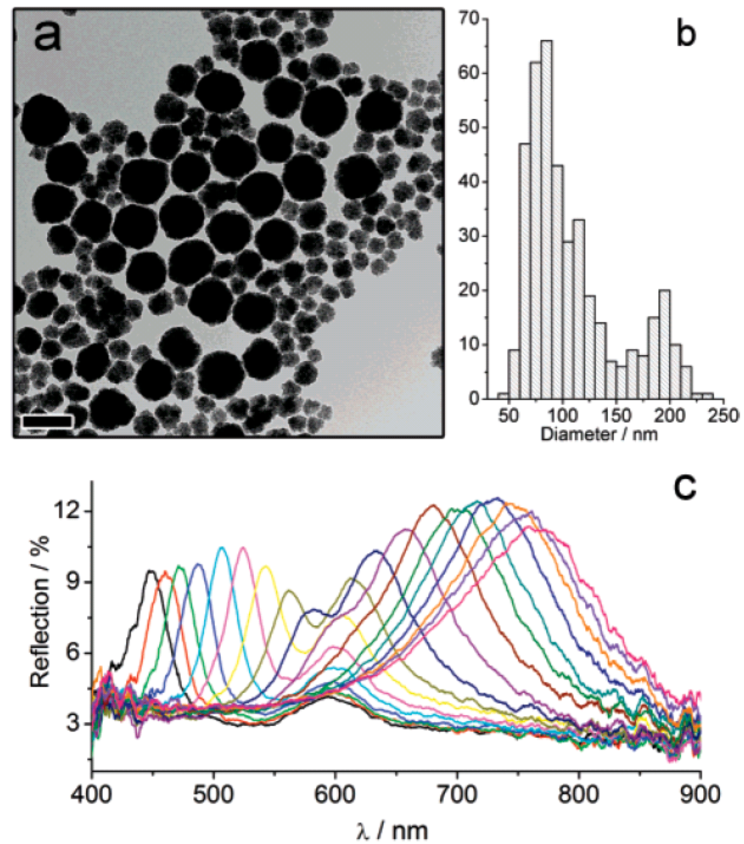
Tuning with bimodal distributions

Mixing similarly sized clusters



75 / 116 nm clusters in 1:1 mass ratio – not a simple overlay, stopbands at intermediate positions relative to individual spectra

Mixing dissimilarly sized clusters
~90 and ~190 nm clusters in 1:2.1 mass ratio



Effectively an overlay of spectra

Weak field - large clusters order
Medium - clusters order independently
Strong - small clusters order

J. Ge, Y. Hu, T. Zhang, T. Huynh, and Y. Yin, *Langmuir* **2008**, *24*, 3671-3680

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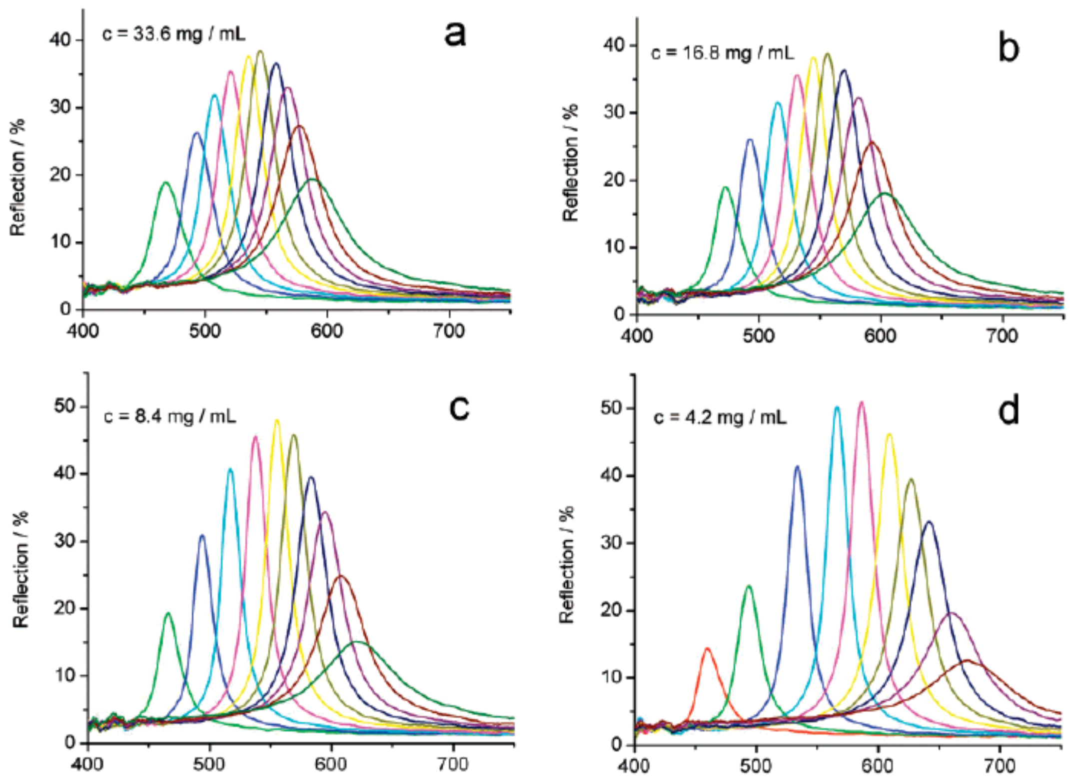
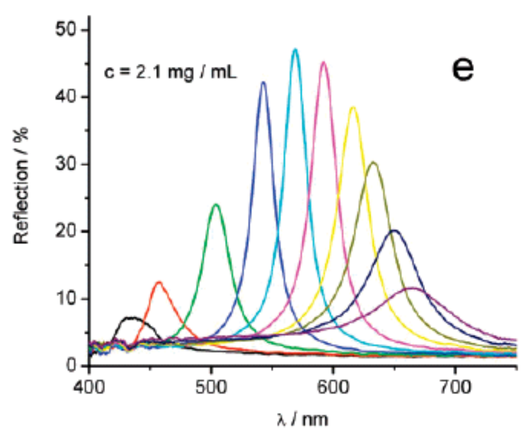
Concentration effects



Higher volume fractions show decreased intensity, possibly due to increased absorption

Optimal diffraction intensity obtained at relatively dilute concentrations

Note: same color, same sample to magnet distance



Dilution accompanied by red shift

Increased electrostatics (decreased conc. of electrolytes)

Stronger fields required for assembly

J. Ge, Y. Hu, T. Zhang, T. Huynh, and Y. Yin, *Langmuir* **2008**, *24*, 3671-3680

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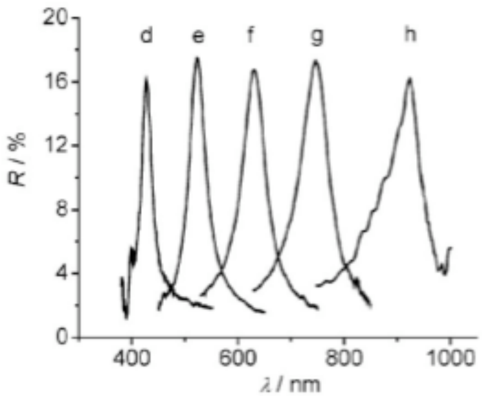
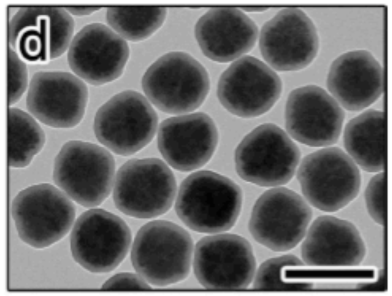
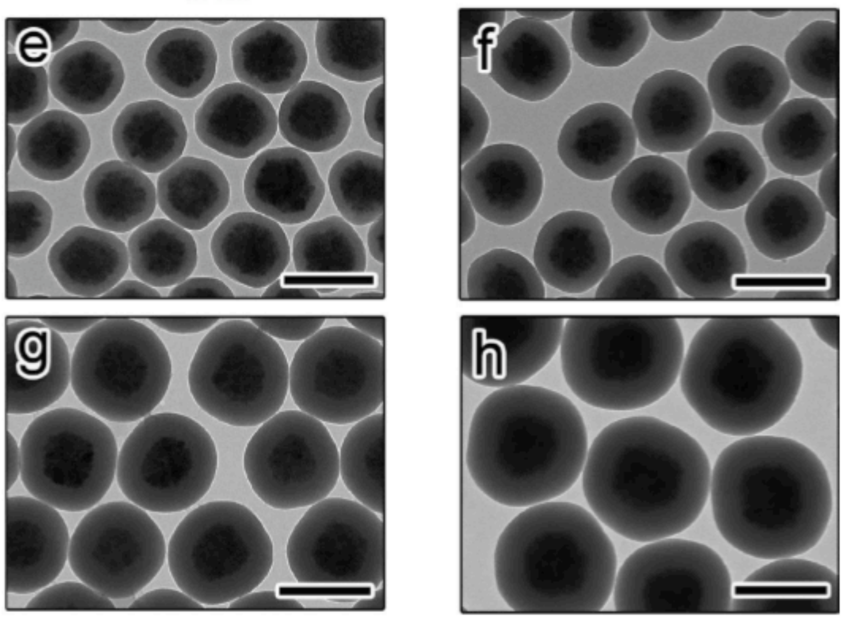
Core/shells for increased tuning range

Max Fe_3O_4 cluster size ~200 nm limits max diffraction wavelength to below 800 nm



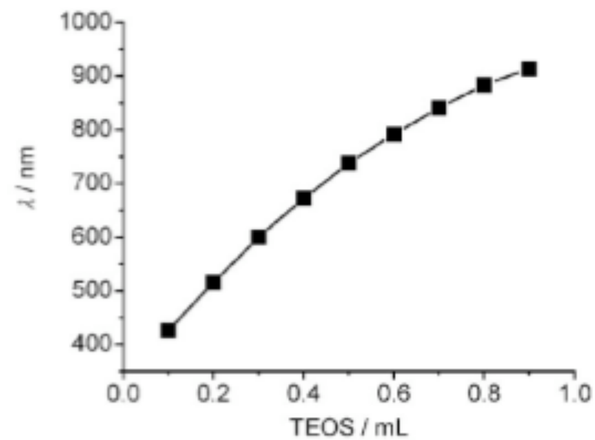
Scale = 200 nm





Hydrolyzing TEOS in presence of clusters produces SiO_2 shell around SPM core

Shell thickness easily controlled



J. Ge and Y. Yin, *Adv. Mater*. **2008**, *20*, 3485-3491

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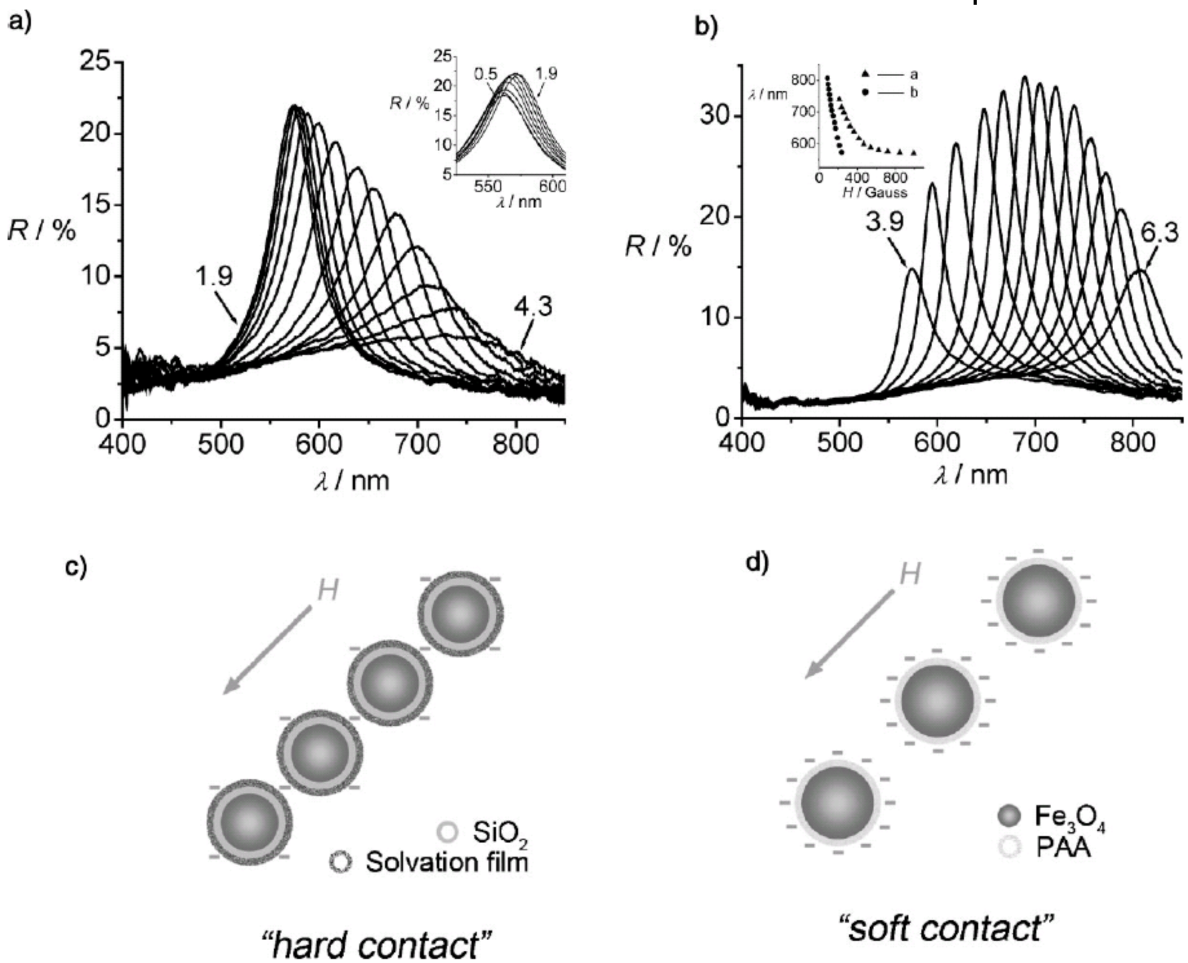
Core/shells change the diffraction profile

170 nm clusters

114 nm Fe_3O_4 core / 28 nm SiO_2 shell in ethanol

170 nm Fe_3O_4 / PAA cluster aqueous



Solvation force provides significant repulsion in non-aqueous solvents

Solvent wets a film on silica surface; disjoining pressure when overlap occurs

Solvation force counters magnetic attraction, leading to skewed profile and "hard contact" conditions

J. Ge and Y. Yin, *Adv. Mater.* **2008**, *20*, 3485-3491

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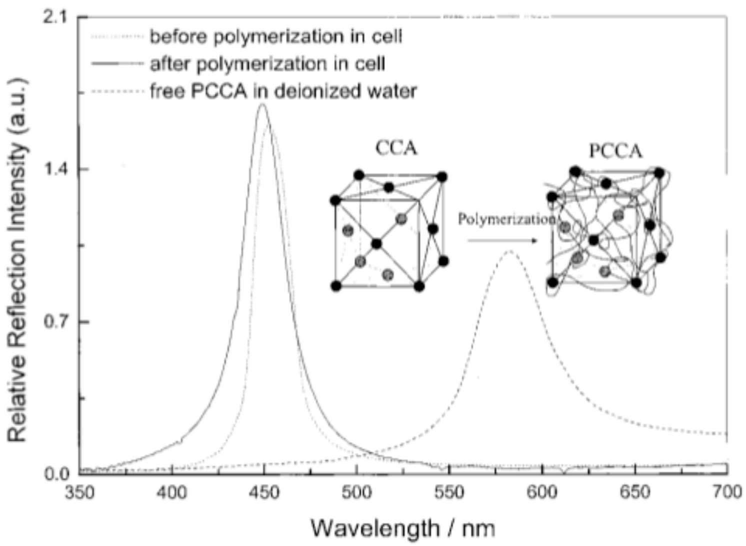
Colloid-polymer composites

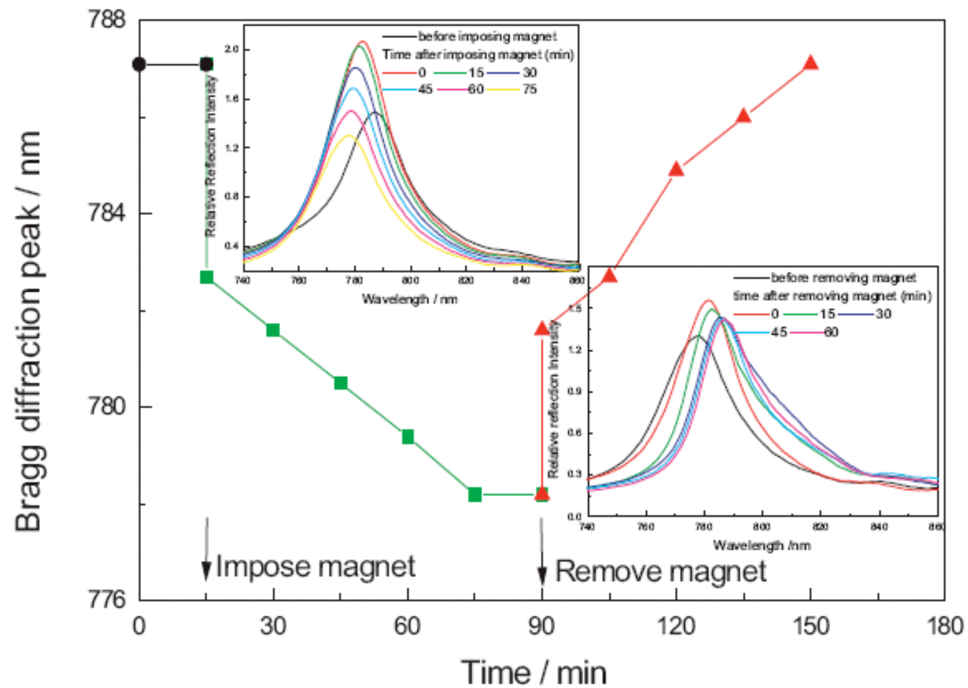
Fe_2O_3-PSt-AM-BAM hydrogel

AM = acrylamide
BAM = *N,N*-dimethylenebisacrylamide



Swells upon hydration, red shift

Fe2O3-PSt-AM-BAM film, 500 μm thick



Very slow response time

X. Xu, G. Friedman, K. D. Humfeld, S. A. Majetich, and S. A. Asher, *Chem Mater*. **2002**, *14*, 1249-1256

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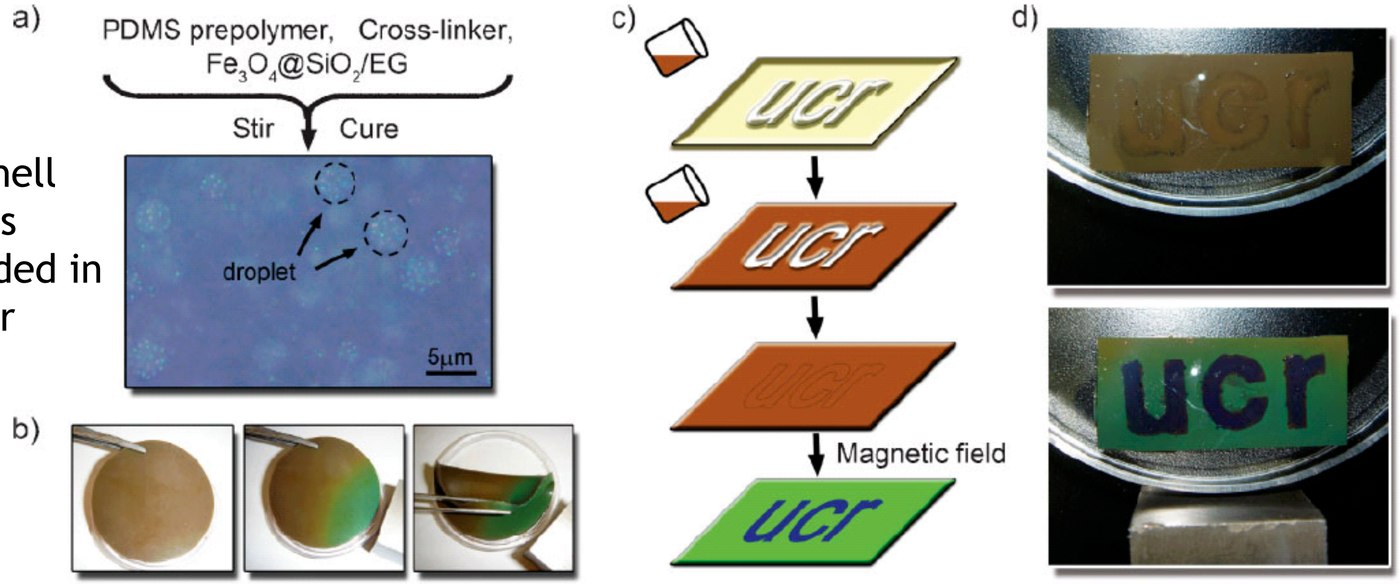
Patterning with Fe_3O_4 PDMS composites

SiO_2 compatibility with organic solvents enables fabrication of highly responsive solid composites

Core/shell droplets embedded in polymer matrix



"Hard contact" condition allows saturation color selection, maximal contrast

Sequential deposition of 110/28 nm and 110/16 nm (core/shell) particles

Polymerize around steel letter templates, remove, repeat in cavities

J. Ge and Y. Yin, *Adv. Mater.* **2008**, *20*, 3485-3491

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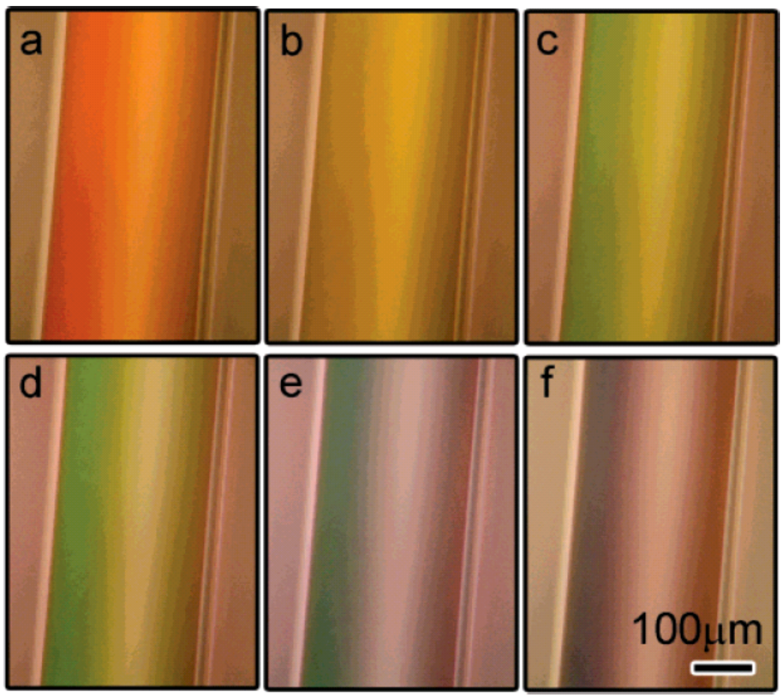
Summary and [potential] applications

Highly tunable and rapidly self assembling superparamagnetic colloidal arrays

Facile optimization with control of preparation and electrostatics (or solvation forces)

Variable tuning profiles with different particle architectures

Straight-forward fabrication of field responsive composite solids



Filters

Waveguides

Sensors

Thin film optics

Magic ink / refrigerator magnets!

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