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, ---> remanence and coercivity.
Preparations - embedded SPM composites

coprecipitation of Fe(II) and Fe(III) chloride with NH₄OH at RT

2-15 nm Fe₂O₃ maghemite (10 nm avg. diameter)

emulsion polymerization

Polystyrene (PSt) - iron oxide composites

No remanence or coercivity at RT

Preparations - Fe$_3$O$_4$ 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

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

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

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

Optical response of PSt-Fe$_2$O$_3$ 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\%

Note the high fields needed to overpower electrostatics

Highly charged surfaces on PSt-Fe$_2$O$_3$ composites, strong electrostatics drive ordering in absence of H.

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


Tuning the interparticle potential

Raising counter ion concentration increases screening

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

Tuning range and particle size

91 nm

108 nm

130 nm

180 nm

Scale bars = 200 nm

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$_3$O$_4$ tuning


Responsive photonic modulation

70 nm Fe$_3$O$_4$ colloids in a periodic magnetic field

a) 0.5 Hz

b) 1 Hz
c) 2 Hz

Tuning with bimodal distributions

- Mixing similarly sized clusters
  - ~75 nm
  - ~116 nm

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

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

Effectively an overlay of spectra

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

Concentration effects

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

Optimal diffraction intensity obtained at relatively dilute concentrations

Dilution accompanied by red shift

Increased electrostatics (decreased conc. of electrolytes)

Stronger fields required for assembly

Core/shells for increased tuning range

Max Fe$_3$O$_4$ cluster size ~200 nm limits max diffraction wavelength to below 800 nm

Hydrolyzing TEOS in presence of clusters produces SiO$_2$ shell around SPM core

Shell thickness easily controlled

Core/shells change the diffraction profile

170 nm clusters

114 nm Fe₃O₄ core / 28 nm SiO₂ shell in ethanol

170 nm Fe₃O₄ / 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

“hard contact”

“soft contact”

Colloid-polymer composites

Fe$_2$O$_3$-PSt-AM-BAM hydrogel

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

Swells upon hydration, red shift

Fe$_2$O$_3$-PSt-AM-BAM film, 500 µm thick

Very slow response time

Patterning with Fe$_3$O$_4$ PDMS composites

SiO$_2$ compatibility with organic solvents enables fabrication of highly responsive solid composites

Core/shell droplets embedded in polymer matrix

Sequential deposition of 110/28 nm and 110/16 nm (core/shell) particles
Polymerize around steel letter templates, remove, repeat in cavities

“Hard contact” condition allows saturation color selection, maximal contrast

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!