Magnetic Iron Oxide Nanocubes – The Effect of Surface Modification on the Formation of a Monolayer

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Introduction

Over the last decade, nanoparticles have become particles of great research interest. Magnetic nanoparticles represent an important class of functional nanoparticles because of their nanoscale properties and size dependent magnetic applications in industries such as environmental, data storage, and biomedical fields. (Wu. et. al; 2016). One of the most prominent features of magnetic Nanoparticles is their size-dependent magnetic properties (Grancharov S. G., et al; 2005). Coercivity is the ability of ferromagnetic material to withstand an external field without being demagnetized. As the size of the nanoparticle decreases, the number of magnetic domains reduces and subsequently, the coercivity of the nanoparticles increases. However, when the size of single-domain particles further decreases below a critical diameter, the coercivity becomes zero, and such particles become superparamagnetic. These particles become magnetic in the presence of an external magnet, but revert to a nonmagnetic state when the external magnet is removed, which avoids 'active' behavior of the particles when there is no applied field.

Size dependent magnetic properties

Magnetic nanoparticles: Preparation, physical properties, and applications in bioscience: February 2012 Nanoscale Research Letters 13(1)144 DOI: 10.1007/s12284-012-0144-0

Goals of the Experiment

- The assembly of magnetic nanoparticles into a monolayer allows their unique behaviors to be harnessed and applied in a variety of industries.
- The formation of Maghemite (γ - Fe_2O_3) into a monolayer has been successful as shown below. However, the formation of Magnetite (Fe_3O_4) nanocubes into a monolayer has not yet been successful (Kim K. S., et al: 2005).

The formation of Maghemite (γ - Fe_2O_3) monolayer

After Ba. Iron Oxide Nanoparticles, Characteristics and Applications: Partner and Operations Manager, Green Nanotech LLC

Goals

- Synthesis of uniform nanoparticles (Fe_3O_4 nanocubes) both in size and shape
- Use of surface modification techniques like annealing, plasma cleaning, and chemical fabrication to enhance even distribution
- Use of spin coating, Langmuir Schaefer and Langmuir Blodgett techniques to facilitate the monolayer formation

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Materials and Methods

- The magnetic iron oxide nanocubes were synthesized using thermal decomposition of Iron(III)Acetylacetonate in the presence of the decanoic acid surfactant preserved in a solution of 3:1 Chloroform: Methanol dispersing agent.
- Then the nanocubes were deposited onto a carbon coated transmission electron microscopy (TEM) grids in order to be controlled and imaged using TEM.
- Before the deposition of the nanocubes, some of the TEM grids were placed in a plasma cleaner in order to remove any organic matter on the grids and to increase the hydrophilicity of the grid. The remaining TEM grids were coated with a layer of heptadecanoic acid using the Langmuir Schaefer and Langmuir Blodgett techniques in order to increase the hydrophobicity of the grids.
- The nanocubes were sonicated using sound energy to remove any aggregates.
- The nanocubes were then spin cast onto the TEM grids at 6000 rpm for 1 minute under nitrogen with a 25 sec waiting time to reduce evaporation variability.
- The plasma cleaned and non plasma cleaned samples were annealed at 100°C and 150°C for time periods of 0.5, 1, 2, 6, 12, 18 and 24 hr.
- Finally, all TEM grids were imaged using transmission electron microscopy.

Results

FTIR spectrum of the magnetic iron oxide nanocubes

Size distribution of Fe_3O_4 nanocubes and a high resolution image of the Fe_3O_4 nanocubes

Results

Plasma cleaned, annealed at 100°C

Plasma cleaned, annealed at 150°C

Not plasma cleaned, annealed at 100°C

Not Plasma Cleaned, annealed at 150°C

TEM Percentage Surface Coverage for different variables

Fe_3O_4 Nanocubes on heptadecanoic acid coated TEM grids

Mag/Conc.	900x	27.5k x
Concentrated		
Diluted		

References

Grancharov S. G., et al. "Bio-functionalization of monodisperse magnetic nanoparticles and their use as biomolecular labels in a magnetic tunnel junction based sensor" *J Phys Chem B*. **2005**; 109(26):13030-13035.

Kim K. S., Park J. K. "Magnetic force-based multiplexed immunoassay using superparamagnetic nanoparticles in microfluidic channel" *Lab Chip*. **2005**; 5(6):657-664

Wu L., et al. "Organic Phase Synthesis of Magnetic Nanoparticles and Their Applications" *Chem. Rev.* **2016**;116. 10473 - 10512

Analysis

- The peak at 579 cm^{-1} confirms the iron-oxygen bond formation in FTIR spectrum
- The nanocubes have a size of around 15 ± 3.5 nm

Annealing:

- The even dispersion of the iron oxide nanocubes is most consistent for the non plasma cleaned TEM grids annealed at 100°C.
- With an increase in temperature, the even dispersion of nanocubes reduces.

Surface Chemistry:

- The non plasma cleaned TEM grids have a more even distribution of nanocubes than the plasma cleaned TEM grids
- The heptadecanoic acid coated TEM grids has a smooth dispersion of nanocubes over the entire TEM grids.

Conclusions

- The Fe_3O_4 nanocubes are stable up to 150°C.
- The non plasma cleaned TEM grids show a more evenly distributed nanocubes layer for 100°C
- The hydrophobic carbon tails on the heptadecanoic acid attract the hydrophobic carbon tails of the decanoic acid coated nanocubes allowing for most even dispersion of nanocubes

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