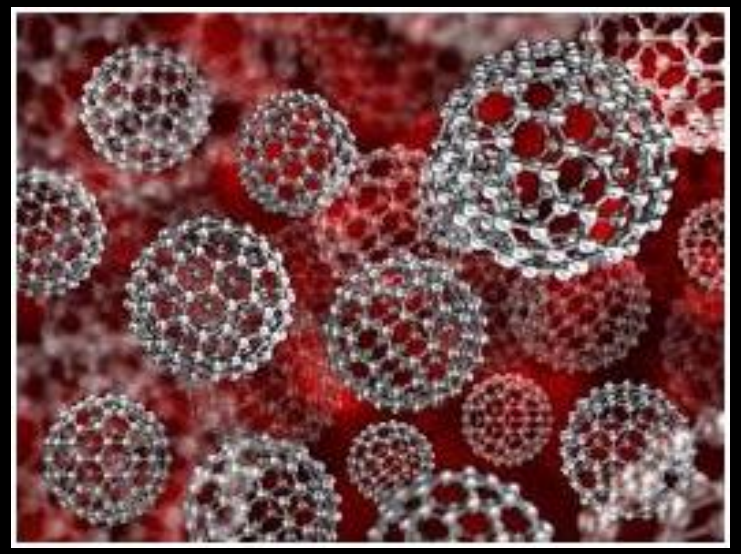
"Superparamagnetic nano-powered separation of micro and nano plastics"



Leisha Martin, PhD

Postdoctoral Research Associate in Marine Biomedical Sciences

Texas A&M University, Corpus Christi, TX, USA

Leisha.Martin@tamucc.edu

TEXAS A&M UNIVERSITY CORPUS CHRISTI

The Plastics Revolution

- Plastics (polymer engineering) has changed the world. Polymers compose tires on your car, your clothing, computer and auto parts, and many more!
- Polymer engineering has revolutionized medicine, cosmetics, research, technology, automotive and many other industries
- Our GDP is highly dependent on exported raw materials
- Plastics production surpasses all other synthetic material production globally
    - 350-400 million metric tons produced annually

The Dark Side of the Revolution

79% of plastic waste is accumulated in landfills or the natural environment[1]

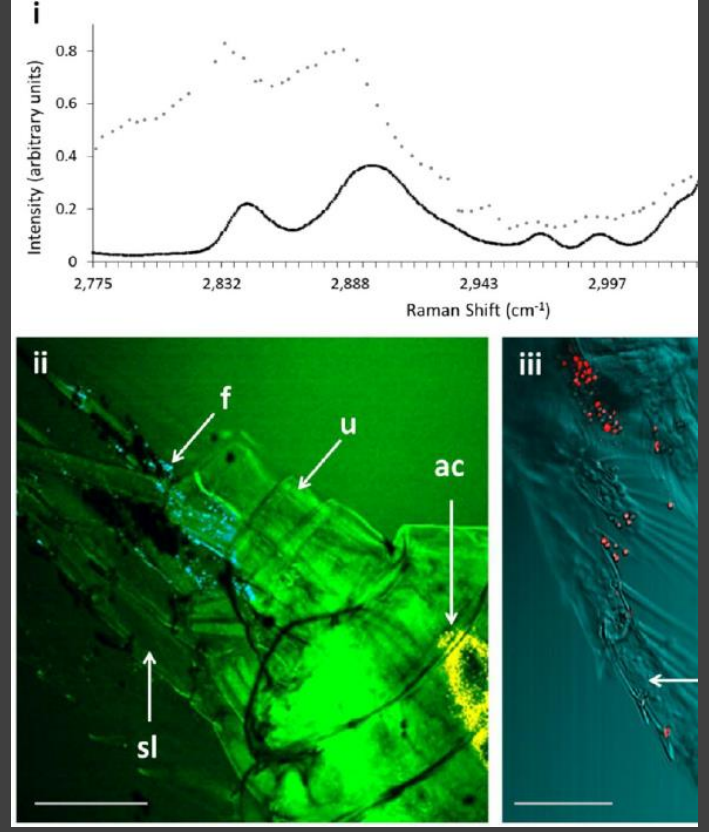
Image by Chris Jordan
https://www.dailymail.co.uk/sciencetech/article-5714369/Filmmaker-captures-heartbreaking-images-albatrosses-killed-plastic-remote-pacific-island.html

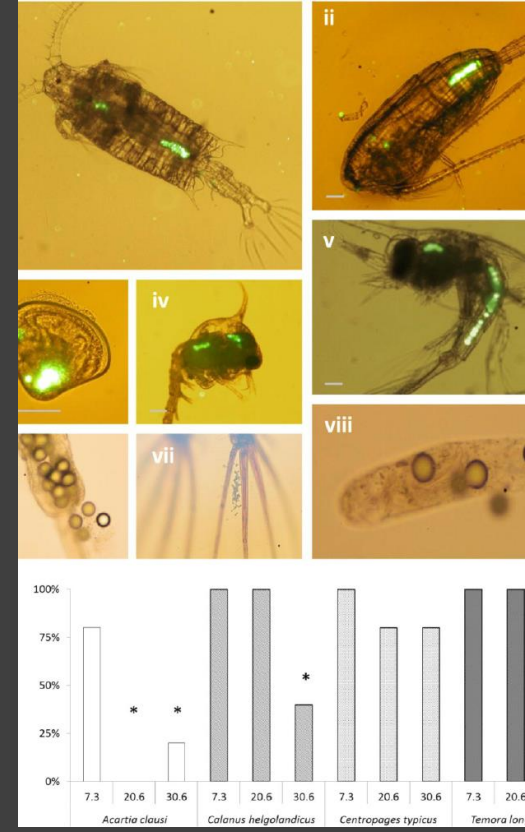
1 Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science advances*, *3*(7), e1700782.

A Closer Look

After disposal and over time, these plastics are fragmented by UV irradiation and mechanical means, into **micro** and **nanoscale** plastic particles (MNPPs) and fibers.[2]

- Upon entering the bodies of organisms, the MNPPs can:
  - cross the blood-brain barrier[3]
  - enter cells[4]
  - exert toxic effects on the immune systems [5,6] and build up in the liver and kidneys [7, 8]
  - Behavioral disorders associated with nanoplastics in the brains of fish have also been reported[9]



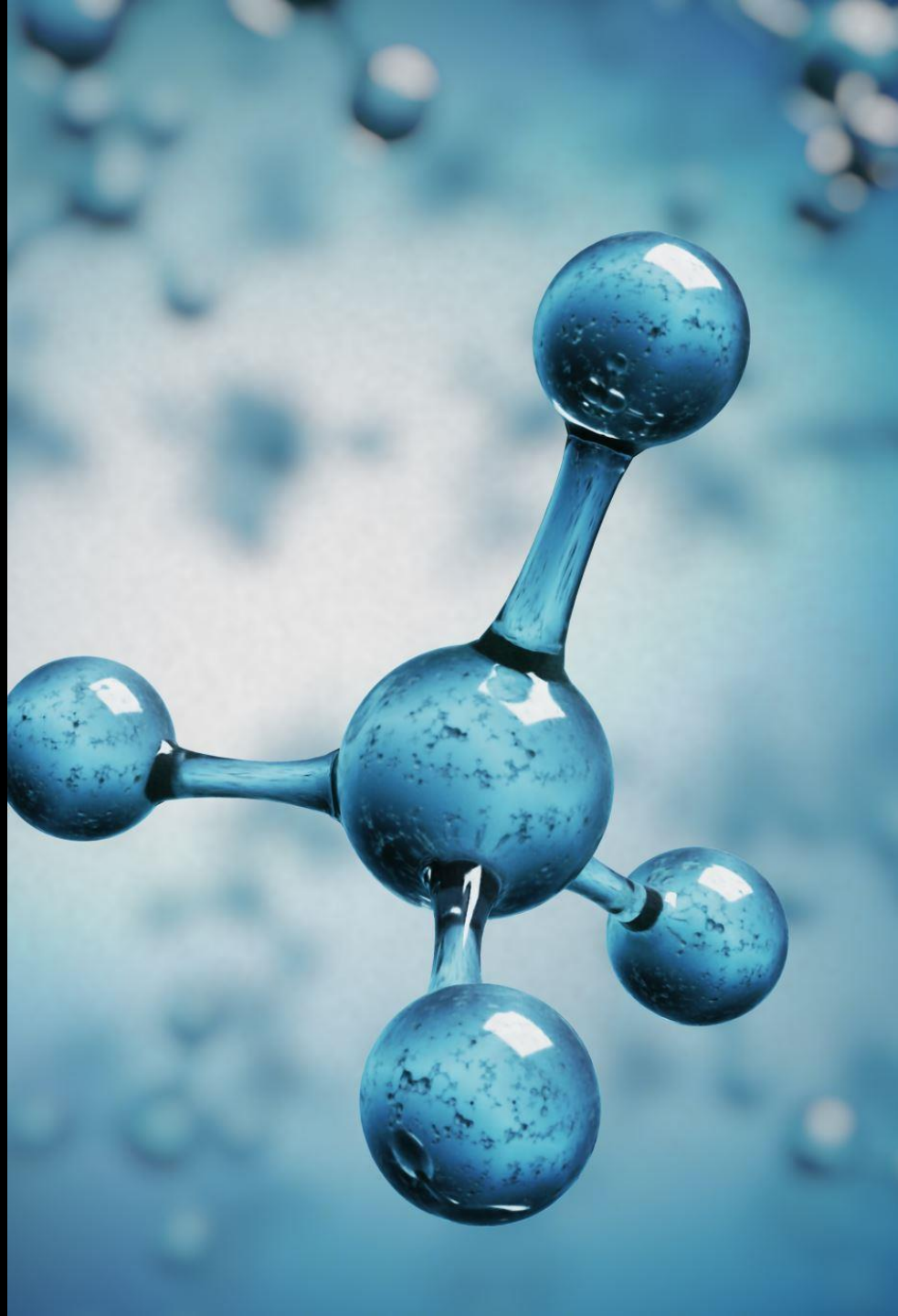


2 Andrady, A. L. (2011). *Marine pollution bulletin*, *62*(8), 1596-1605.
3 Chen, Q., et al. (2017). *Science of the total environment*, *584*, 1022-1031.
4 Vogt, A., et al. (2006). *Journal of investigative dermatology*, *126*(6), 1316-1322.s
5 Greven, A. C., et al. . (2016). *Environmental toxicology and chemistry*, *35*(12), 3093-3100.
6 Brandts, I., et al. (2018). *Genomics*, 110(6), 435-441.
7 Gundersen, G. A. (2019). Master's thesis, NTNU.
8 Rubio, L., et al. (2020). *Journal of Toxicology and Environmental Health, Part B*, *23*(2), 51-68.
9 Mattsson, et al. (2017). *Scientific Reports*, *7*(1), 1-7.

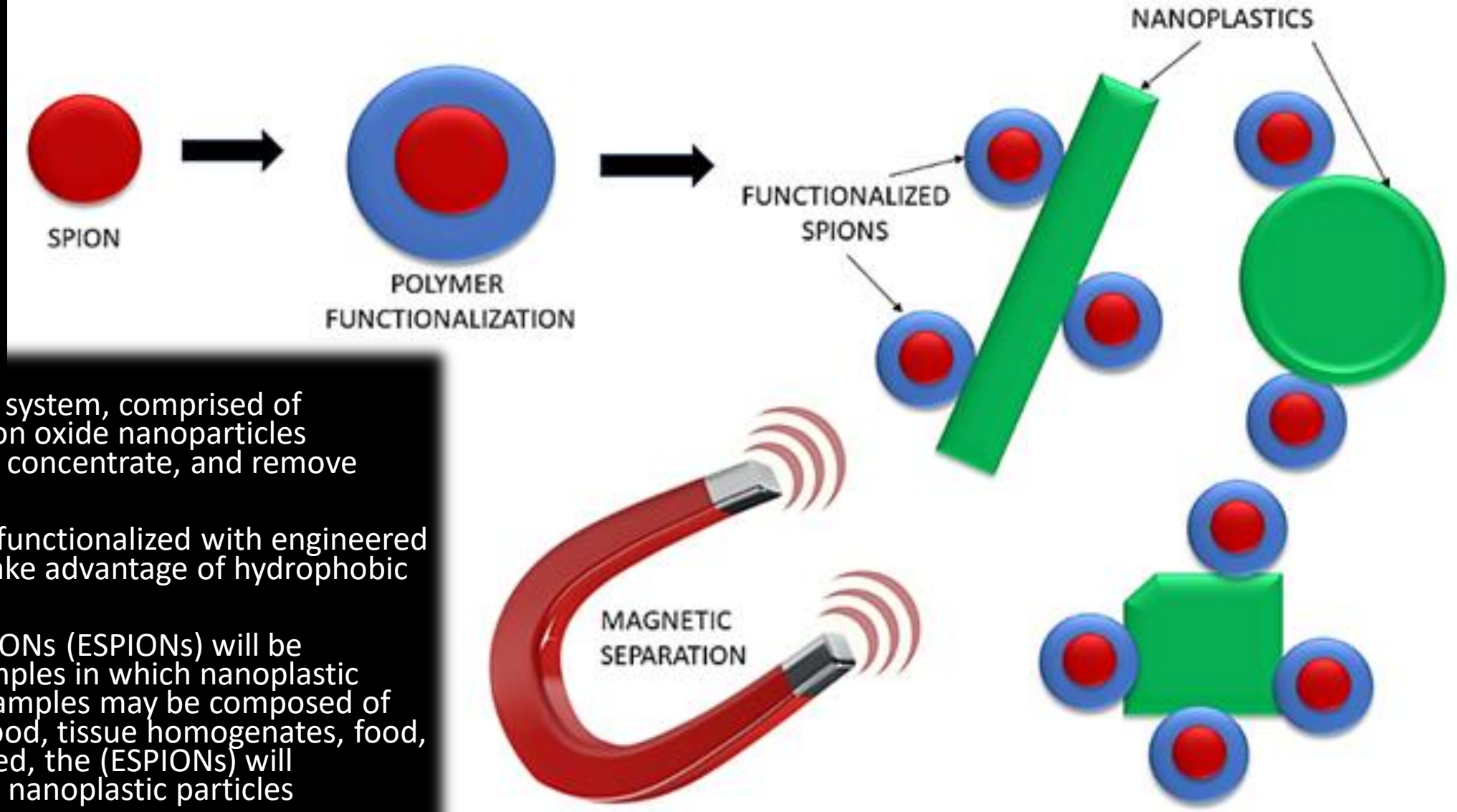
Upper Images: Cole, Matthew, et al. *Environmental science & technology* 47.12 (2013): 6646-6655.
Lower Image: https://www.triplepundit.com/story/2018/our-plastic-problem-plastics-marine-life-and-beyond/11841

Separation of Nano/Micro Plastics

- Current methods for the separation of microplastics have lower size limitations
- Filtration must be incremental (by size) to avoid clogging of filters and membranes. Very small membrane filtration is time consuming. Particles may remain adhered to filters
- Density separations are limited to larger microscale particles due to the hurdles of removing very small particles from the air-solvent interface
- Low density materials are not easily separated by centrifugation
- Polymers are temperature sensitive making evaporation difficult
- Successful laboratory methods may not be easily “scaled up”



ESPION Separation



Novel nanocomposite system, comprised of superparamagnetic iron oxide nanoparticles (SPIONS), to separate, concentrate, and remove MNPPs

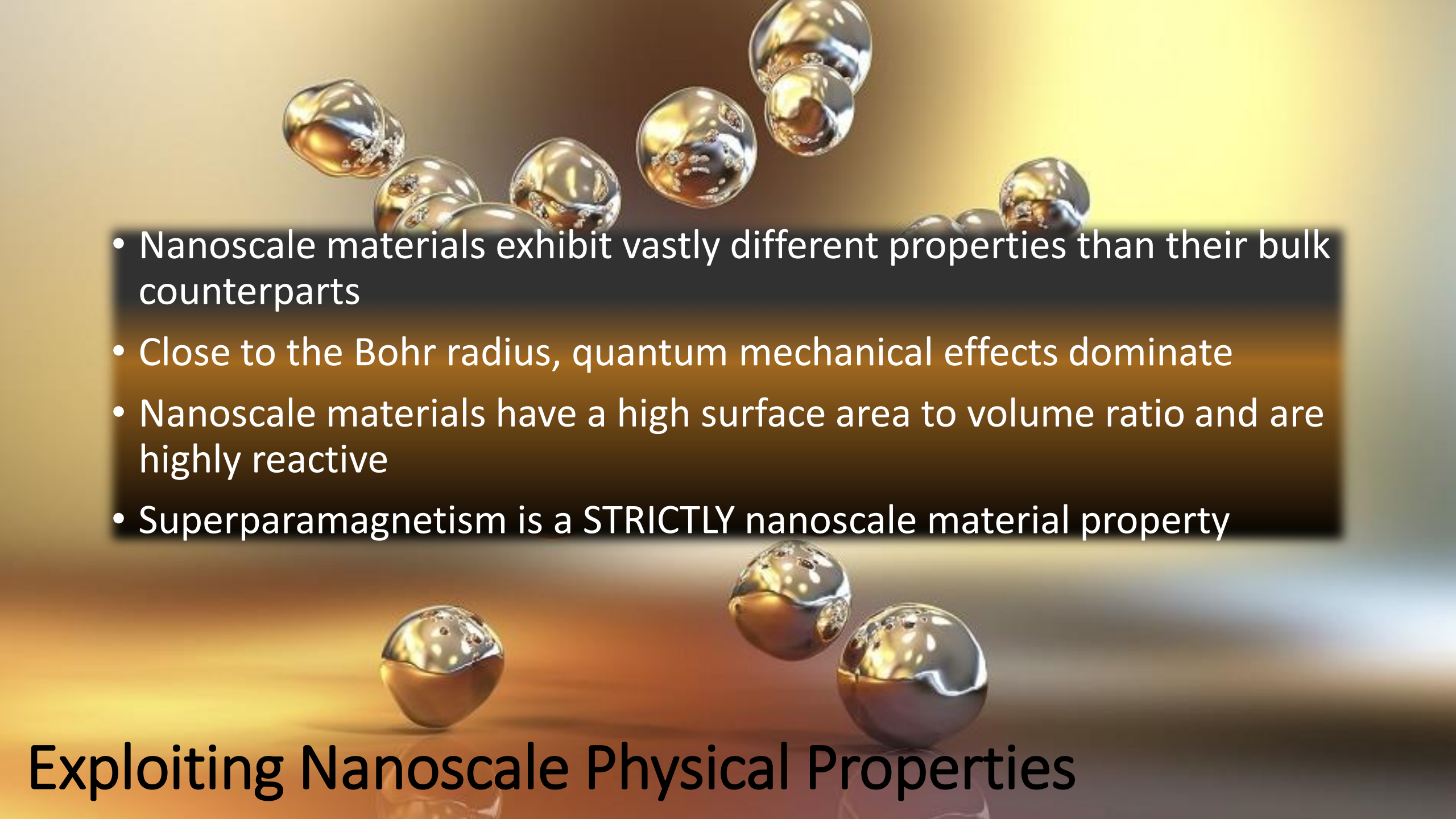
1) The SPIONs will be functionalized with engineered polymer coatings to take advantage of hydrophobic agglomeration

2) The engineered-SPIONs (ESPIONs) will be dispersed into the samples in which nanoplastic detection is sought. Samples may be composed of salt or fresh water, blood, tissue homogenates, food, and more. Once applied, the (ESPIONs) will selectively bind to the nanoplastic particles

3) The ESPIONs, having remotely controlled magnetic properties, will be activated by an external magnetic field, allowing for magnetic separation of the ESPION-nanoplastic heteroaggregates.

Synthesis of Superparamagnetic Iron Oxide Nanoparticles (SPIONs)

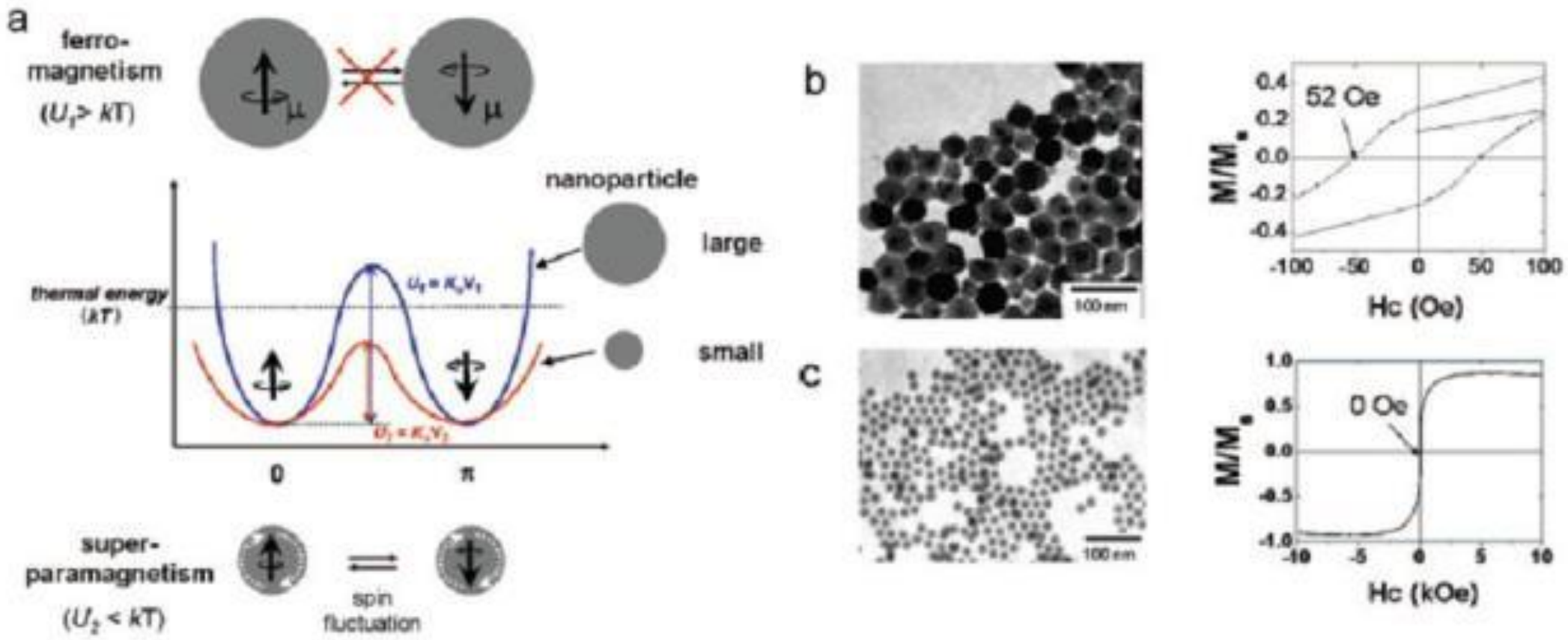
- Green chemistry solvothermal method using water-soluble iron salts under air-free conditions
- Major reagents is oleic acid (the major component of olive oil)
- Some modifications make use of coconut oil, beeswax, or other natural oils, as opposed to petroleum products
- Resulting material is composed of magnetite, hematite and wüstite phases of iron oxide
- SPIONs exhibit low cytotoxicity in eukaryotic cells, similar to that of naturally existing iron polymorphs or elemental iron



- Nanoscale materials exhibit vastly different properties than their bulk counterparts
- Close to the Bohr radius, quantum mechanical effects dominate
- Nanoscale materials have a high surface area to volume ratio and are highly reactive
- Superparamagnetism is a STRICTLY nanoscale material property

Exploiting Nanoscale Physical Properties

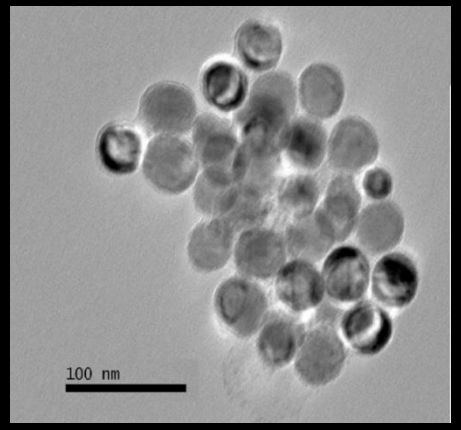
Superparamagnetism



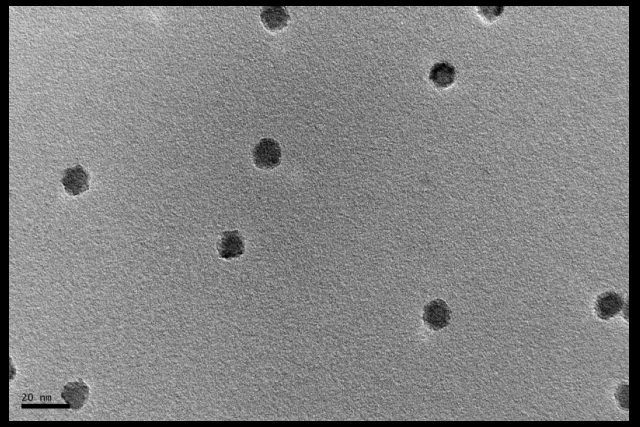
Size dependent energy diagram and transition of magnetic nanoparticles:
-. Ferromagnetism in a large particle (top)
-. Superparamagnetism in a small nanoparticle (bottom)

Characterization of Spherical SPIONs

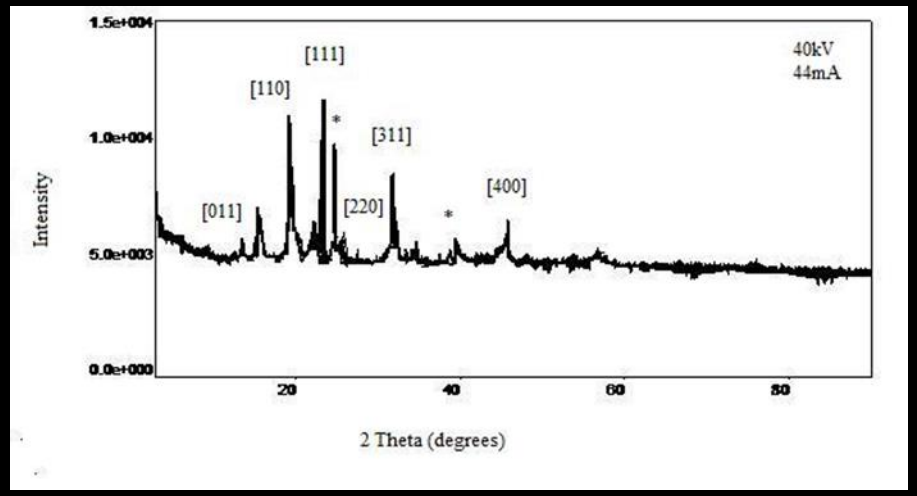
- Spheres are highly monodisperse ±1.4nm
- Sizes between 18-25 nm are produced, depending on reaction time



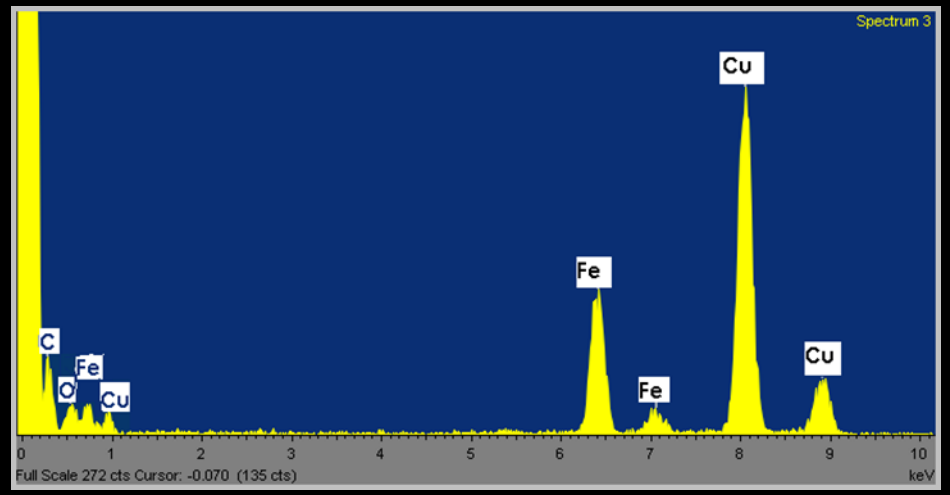
HRTEM *Scale bar 100 nm*



HRTEM *Scale bar 20 nm*

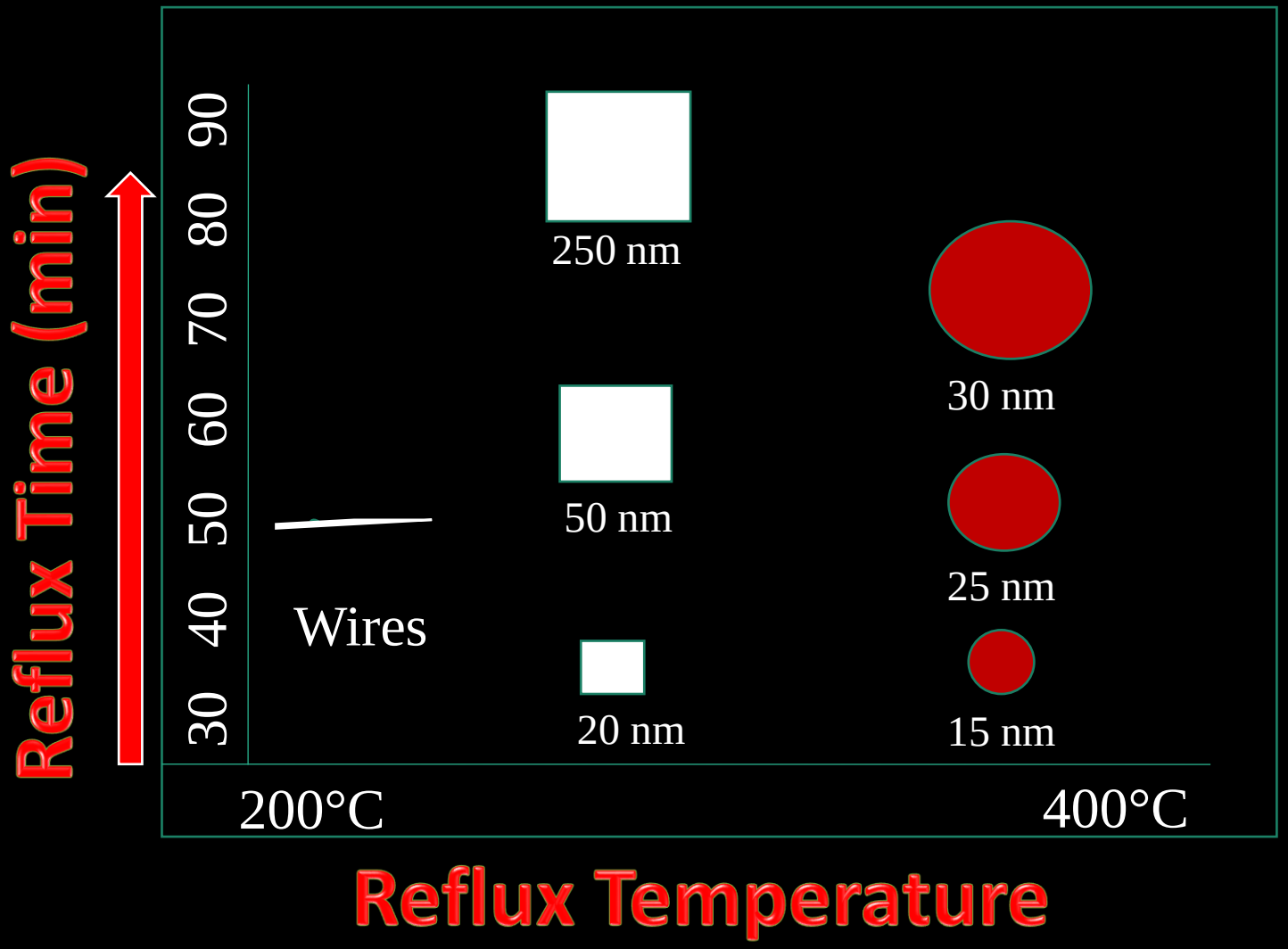


XRD spectrum FCC (Fd3m) crystal ~70% Fe3O4

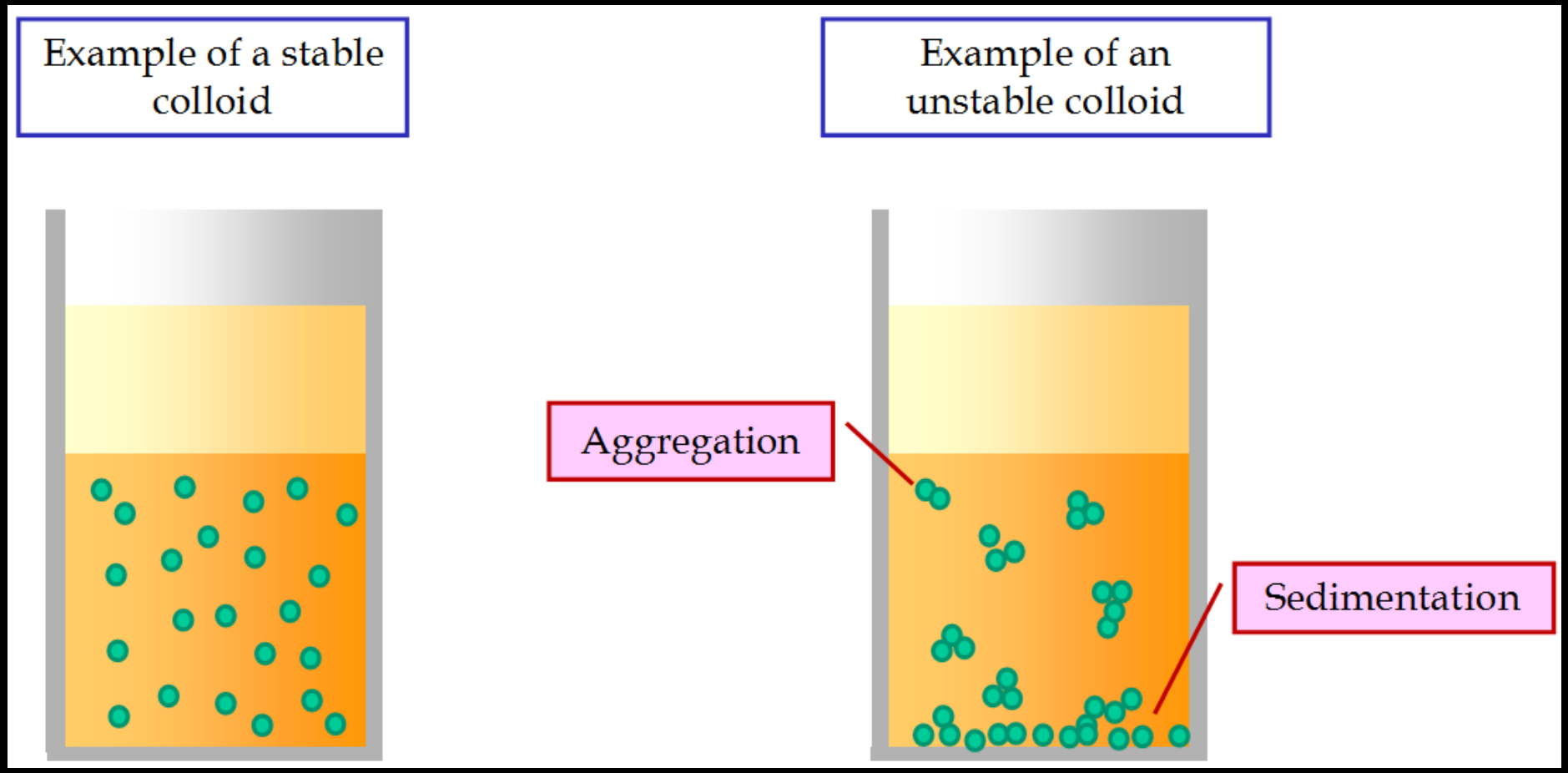


EDS Spectrum shows elemental composition

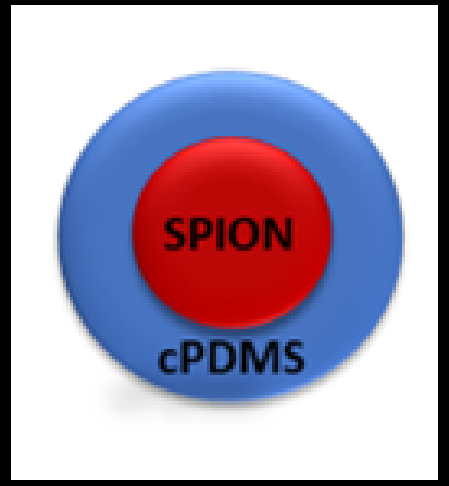
Formation of Different Sizes and Morphologies

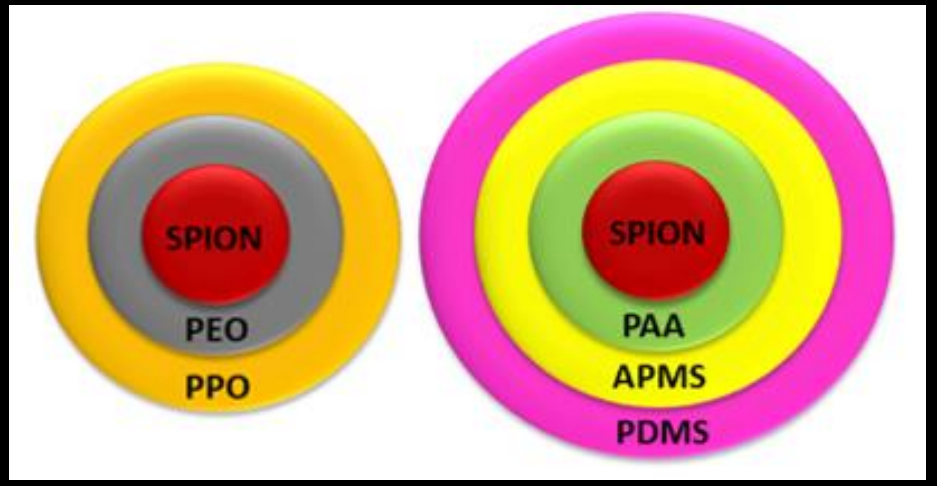


Colloidal Stability



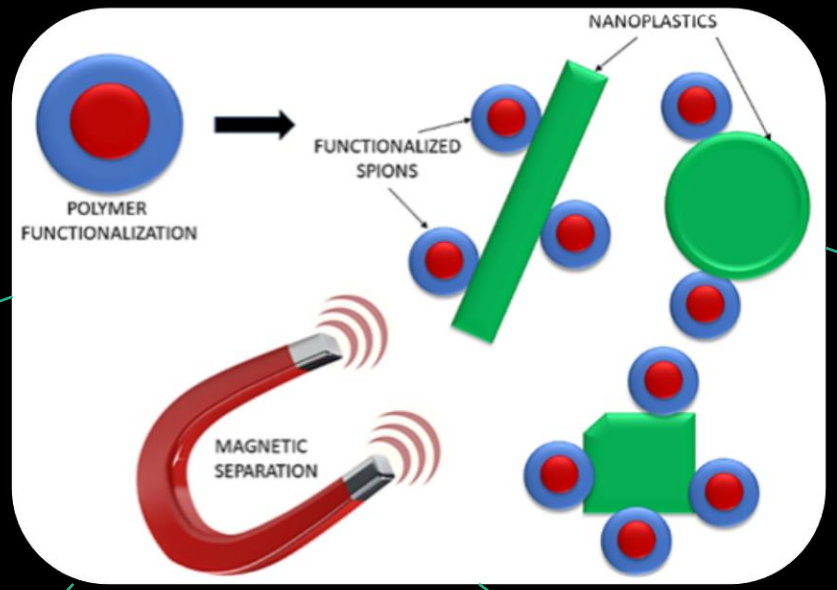
Nanocomposite Functionalization & Mussel-Inspired Chemistry

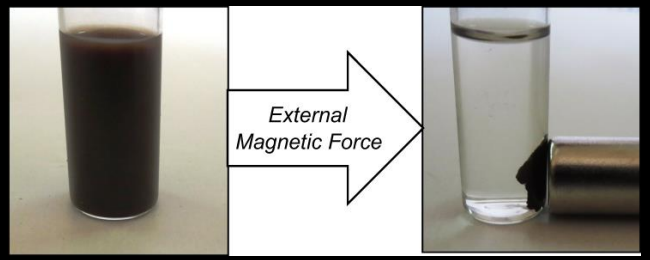




Methods for Removal of Heteroaggregates from Solvent

Centrifugation





External Magnet Force

www.belki-filtration.com/products/magnetic-filter/

Magnetic Filters or Membranes

High gradient magnetic separators (HGMS) and wet high intensity magnetic separators (WHIMS)
www.slon.com
Shown: SLON 100 bench top WHIMS

Questions?