

Polymer Superparamagnetic Iron Oxide Nanorattles

Duc Nguyen¹, Tim Davey²
and Brian S Hawkett¹

¹ Key Centre for Polymers and Colloids, School of Chemistry and
University of Sydney Nano Institute, The University of Sydney, NSW
2006, Australia

² Dulux Australia, 1970 Princess Highway, Clayton, Victoria 3168,
Australia



Research in the KCPC-Hawkeitt group

Within KCPC we have been doing collaborative and contract research for industry for over 22 years

Disperse Phase Polymerization and Coatings
ARC & DuluxGroup Australia

Recycled HDPE materials and liquid waste
 • **PEGRAS**
 • **NSSN**
 • **Visy**
 • **Labelmakers**
 • **Bega/Dairy Farmers**

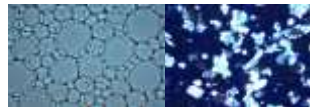
Battery technology for energy storage
 • **Gelion**
 • **Nexeon**

Microplastic removal from wastewater
 • **PEGRAS**
 • **NSSN**
 • **NSW health**



The Hawkeitt Group

Explosive Emulsions for the Mining Industry



ARC & Dyno-Nobel Asia Pacific

Sterically stabilized nanoparticles for nano medicine



- **Sirtex Medical**
- **Ferronova**
- **Zeta Therapeutics**

Agrochemical Delivery Systems
Syngenta Crop Protection



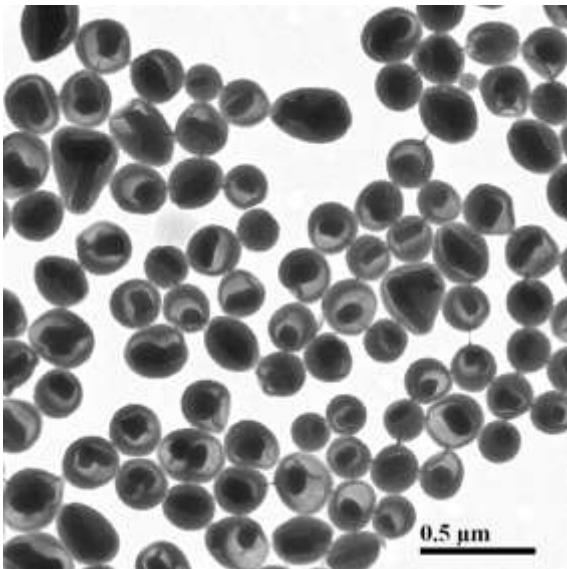
Ionic Liquid Ferrofluids for Space Propulsion



AOARD, US Air Force, Michigan Tech and Yale

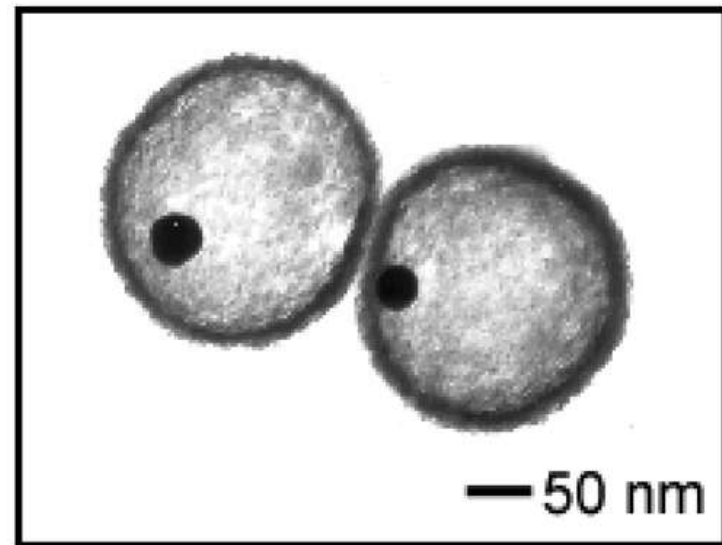
Nanorattles

- Nanoparticles consist of:
 - A hollow shell encapsulating
 - An (in)organic core
 - With a water/air layer/void separating the shell and the core



TiO₂ polymer nanorattles

Journal of Polymer Science Part A:
Polymer Chemistry 50 (2), 346-352

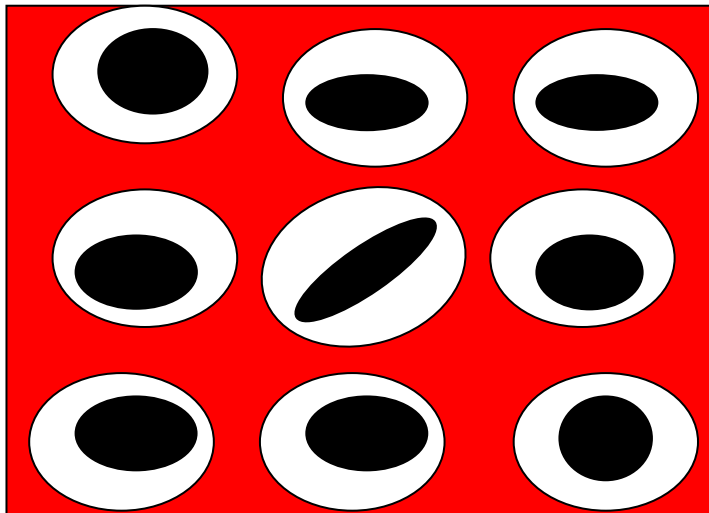


Gold polymer nanorattles

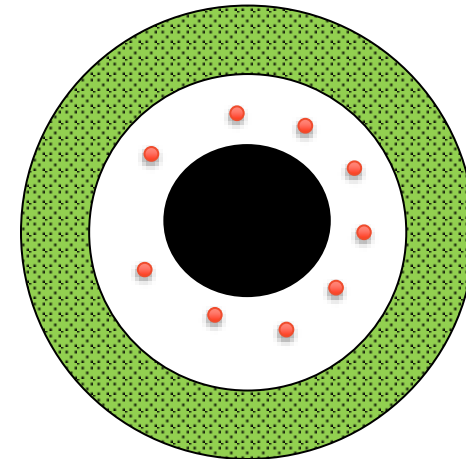
J. Am. Chem. Soc. 2003, 125, 9, 2384–2385

Potential applications

- Paint and coating: enhance opacity of titanium dioxide in paint films, resulting up to 40% pigment saving
- Potential applications:
 - Drug delivery: space between the shell and core can be used to store drugs, especially anti-cancer drugs
 - Catalysis/battery: Adv. Mater.2008,20,3987–4019



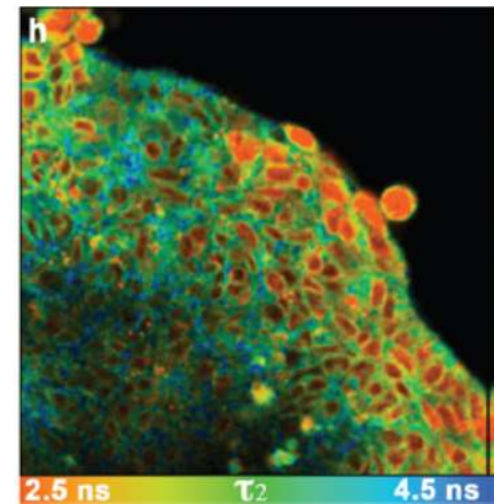
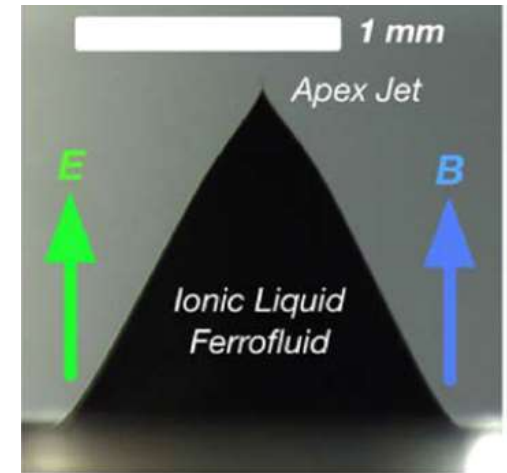
Nanorattles in paint film to enhance pigment light scattering



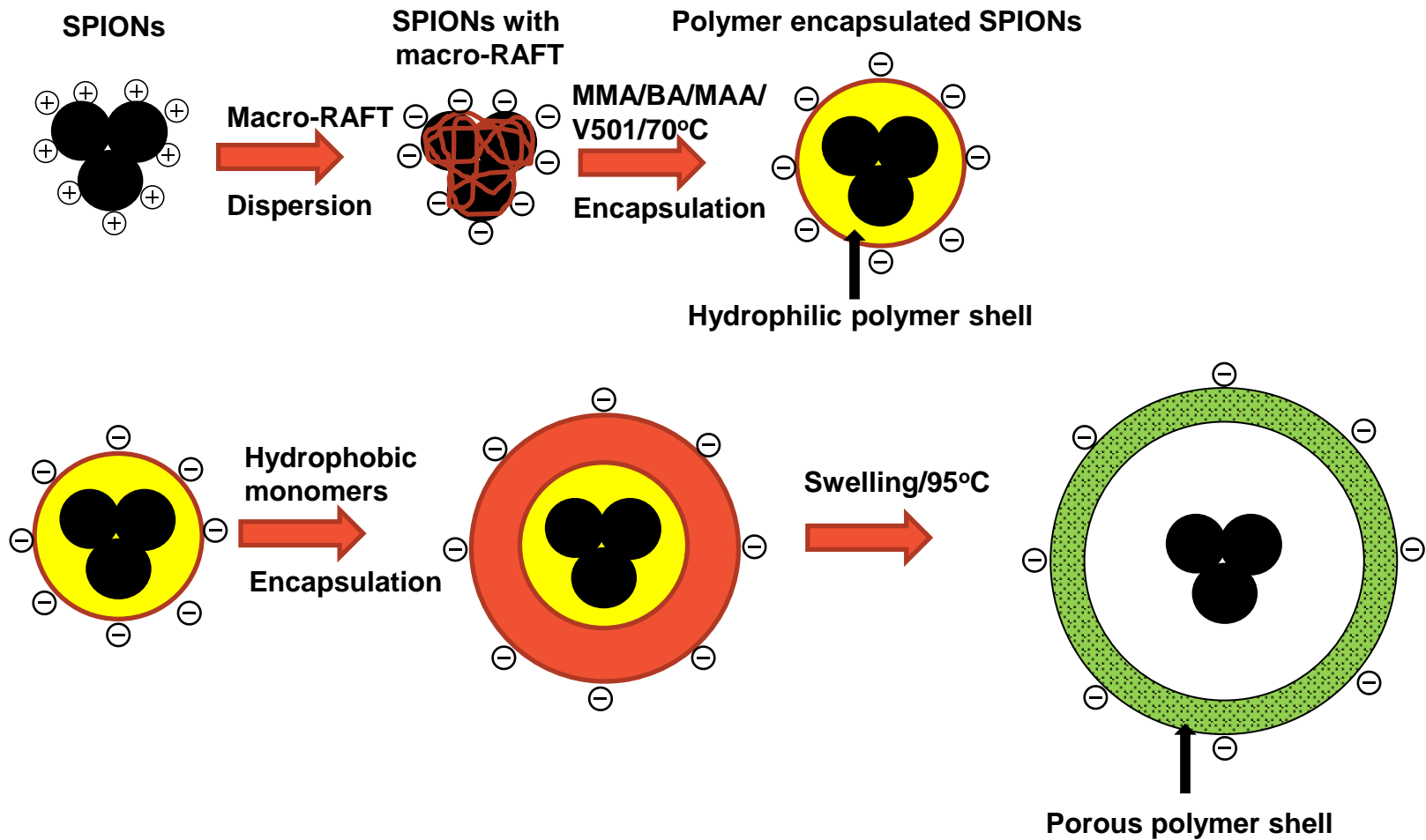
Drug loaded nanorattles

SPION core

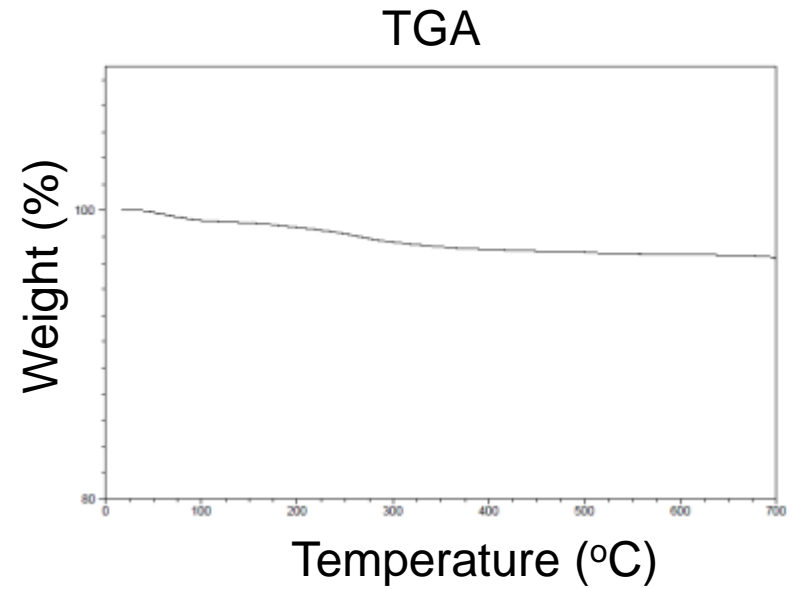
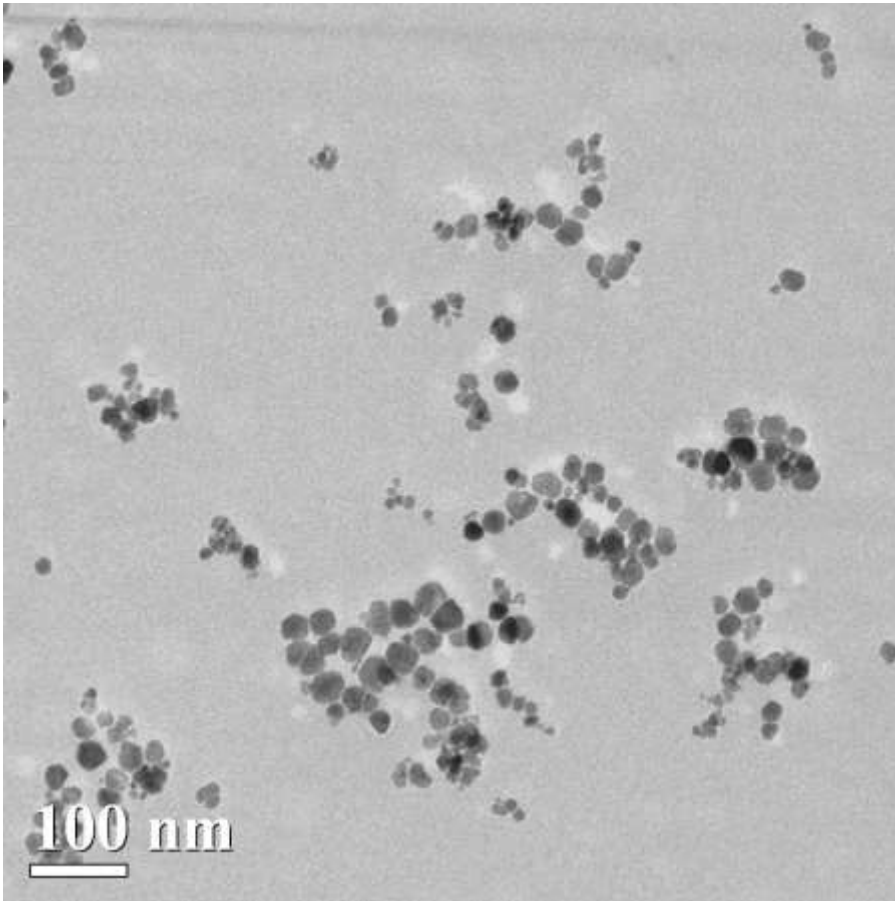
- Superparamagnetic iron oxide nanoparticles (SPIONs): display magnetic property only under the influence of magnetic fields
- Iron oxides:
 - Magnetite: Fe_3O_4
 - Maghemite: Fe_2O_3
 - Iron oxides doped with other metal oxides
- They have been used in a number of biomedical applications such as:
 - Cell labeling
 - Hyperthermia
 - Drug delivery
- We wanted to make iron oxide nanorattles:
 - To cover the IP that we launched with Dulux
 - Sirtex (customer at the time) was interested in SPIONs
 - SPIONs are ideal for targeted delivery



SPION nanorattle synthesis via RAFT emulsion polymerisation

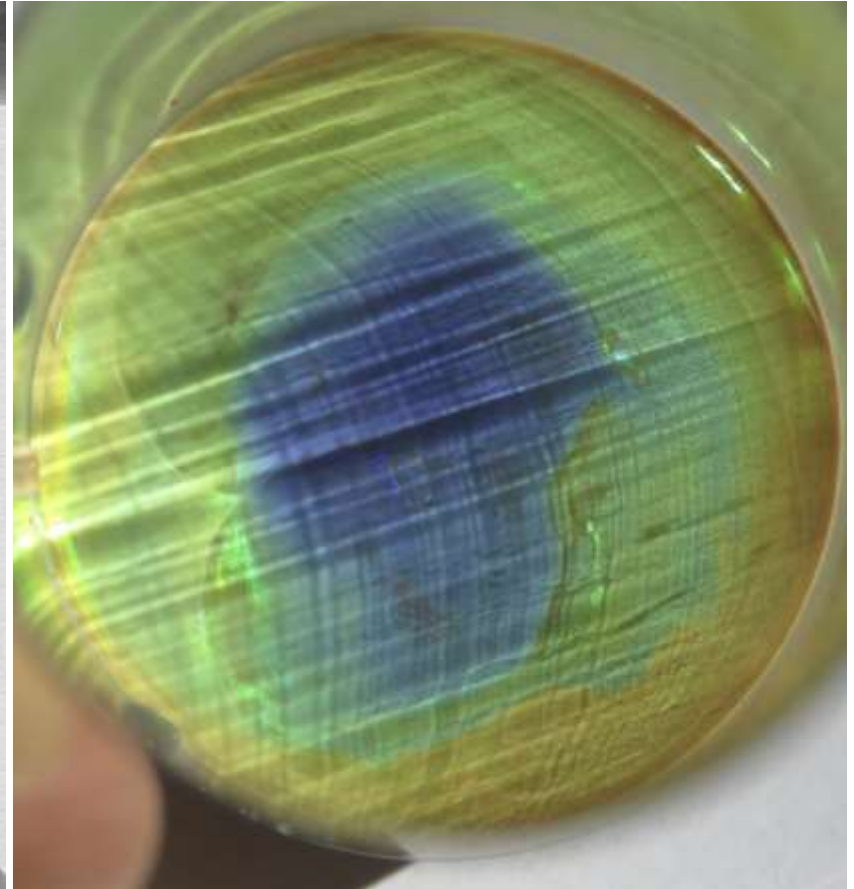
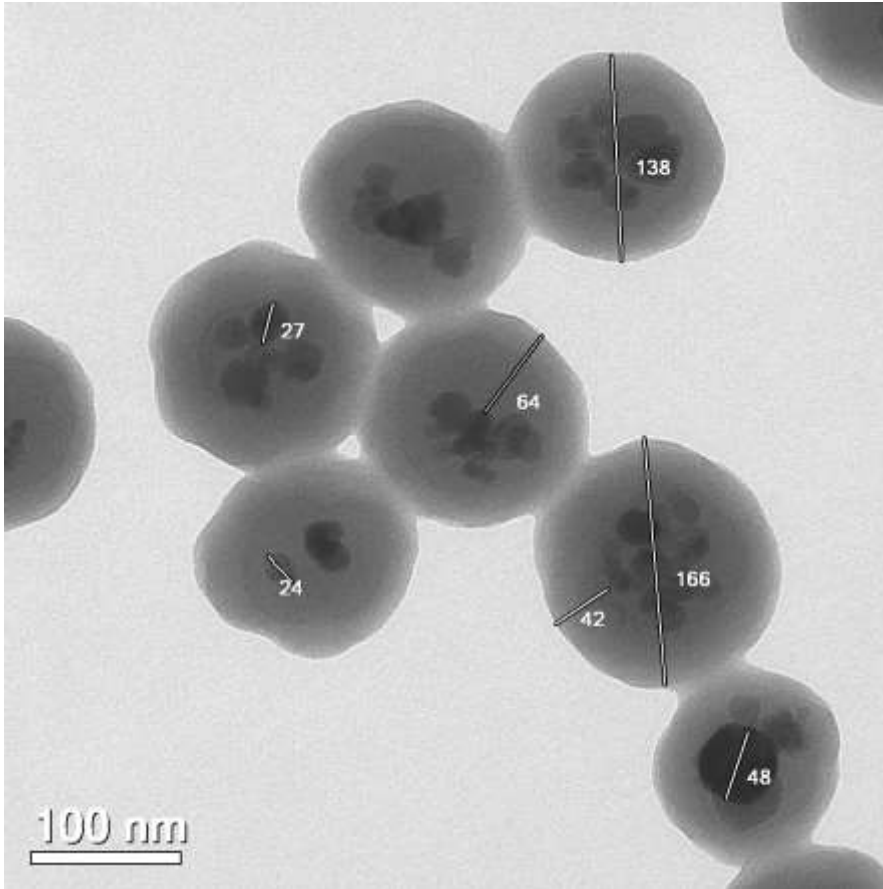


SPIONs

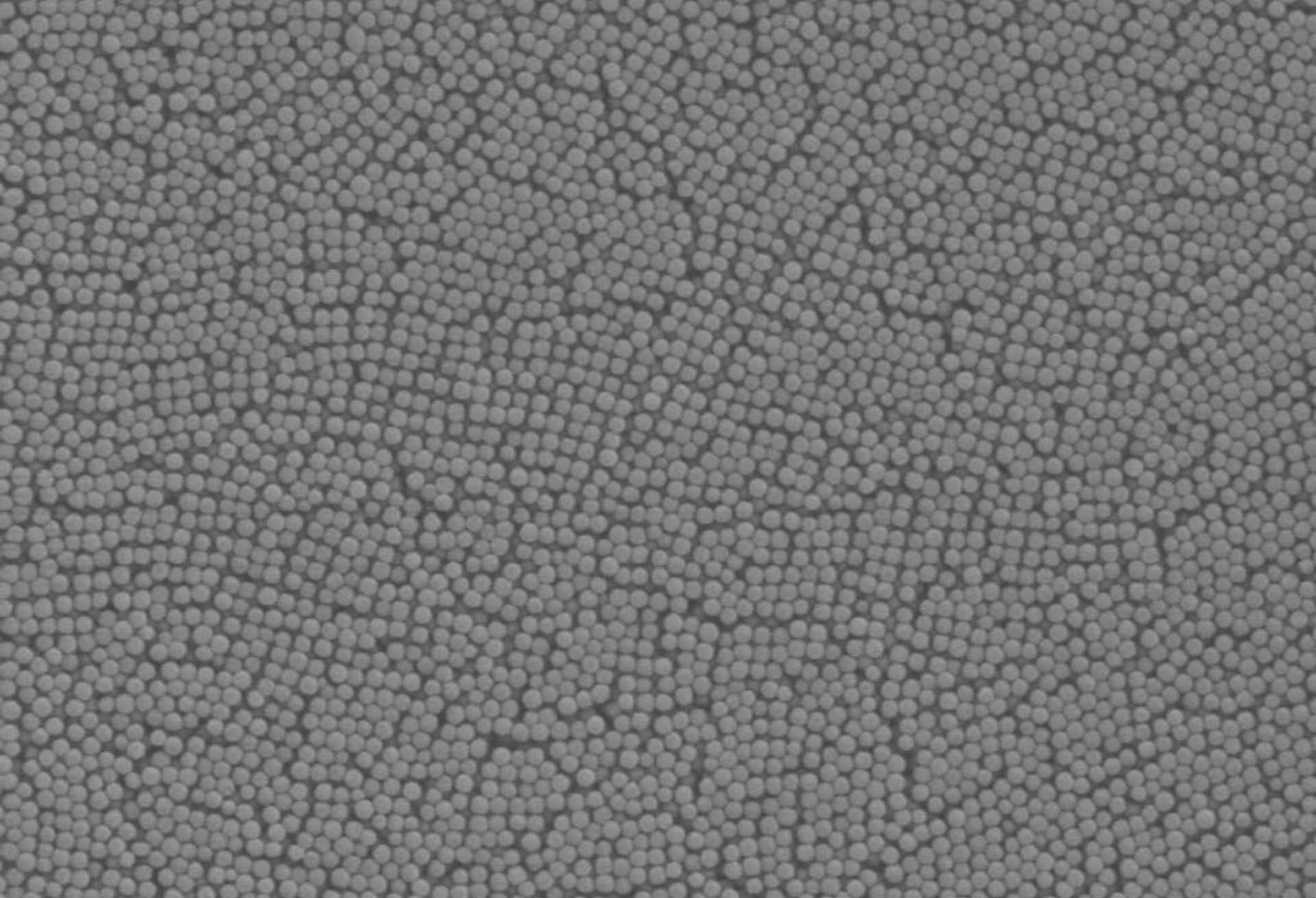


- Sirtex iron oxide nanoparticles are 10-50 nm in diameter with strong magnetic property
- TGA: no organic stabilizer

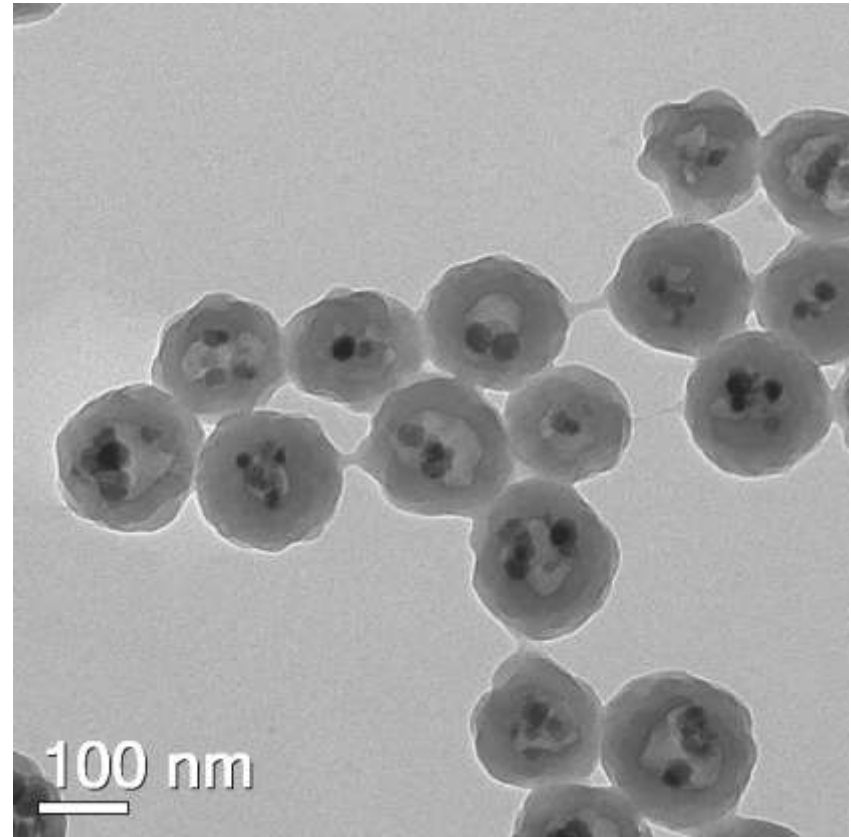
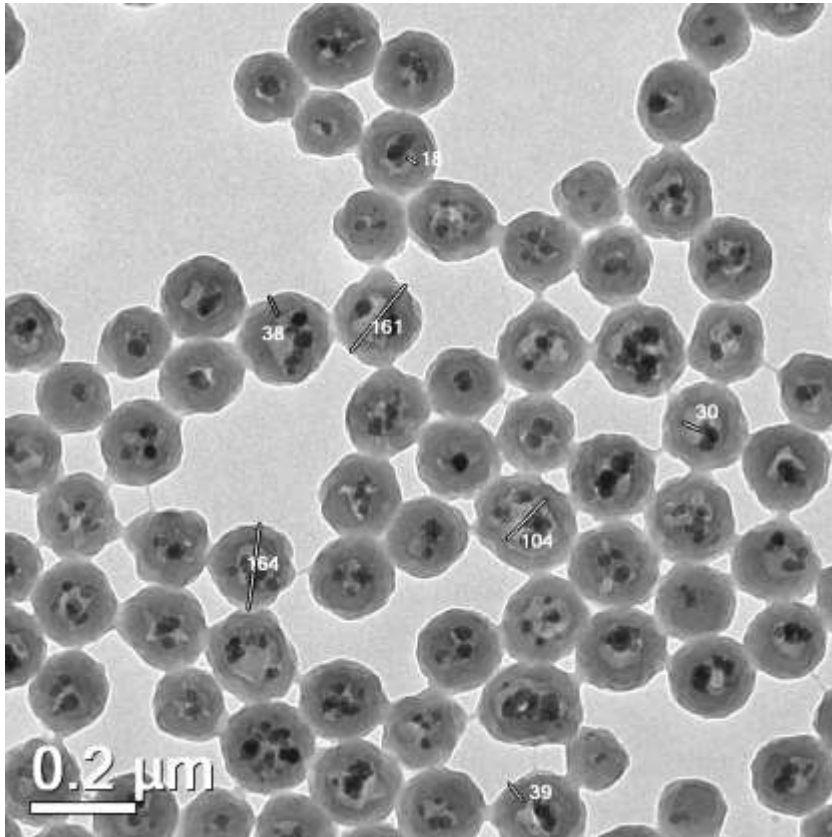
Polymer encapsulated SPIONs (before swelling)



- 150 nm on average, 55 nm shell thickness
- Monodisperse and opalescence

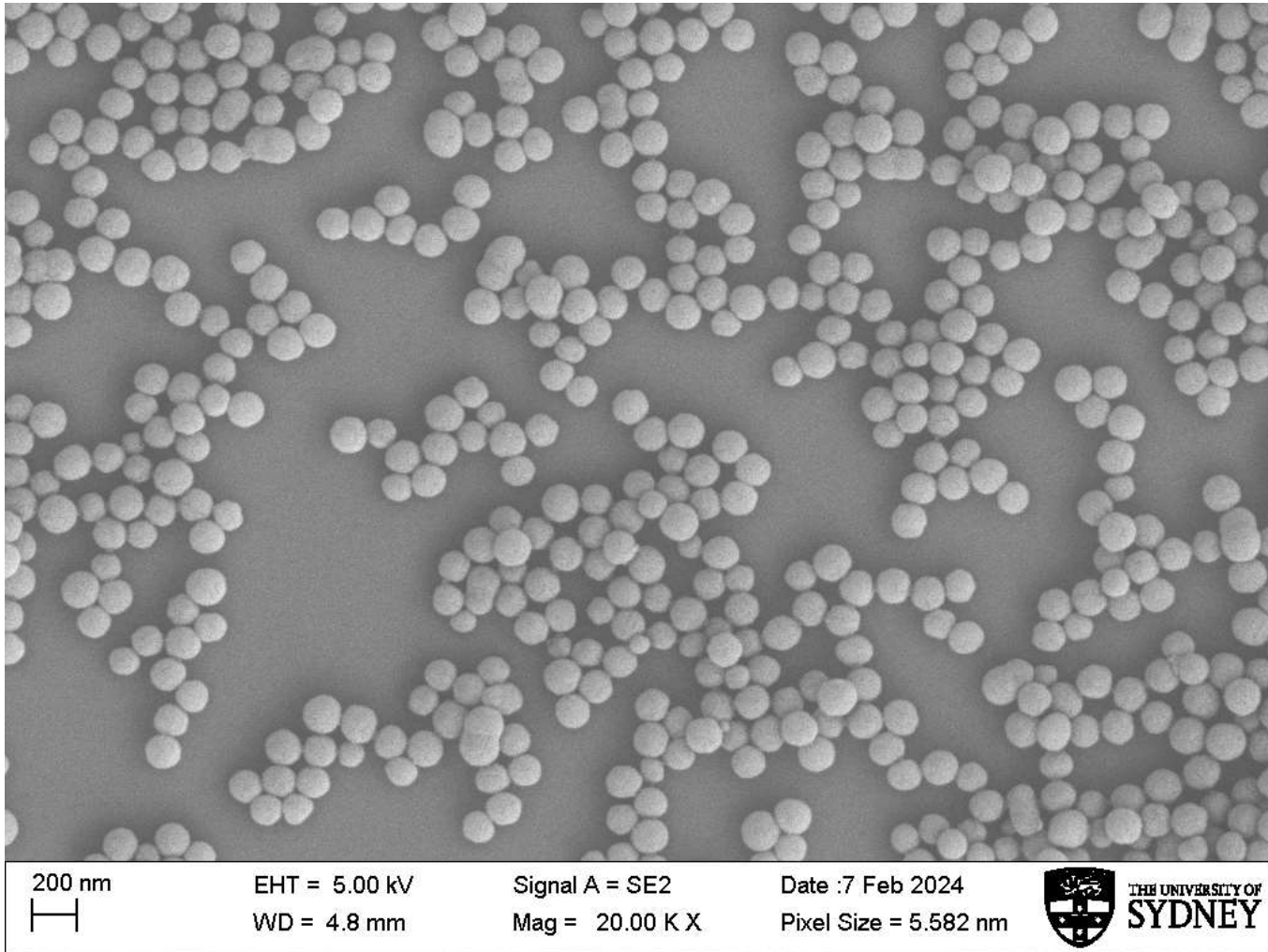


SPION polymer nanorattles (TEM)



- 185 nm on average (DLS, 0.004 PDI)
- 40 nm shell thickness
- 50-100 nm voids containing iron oxide particles

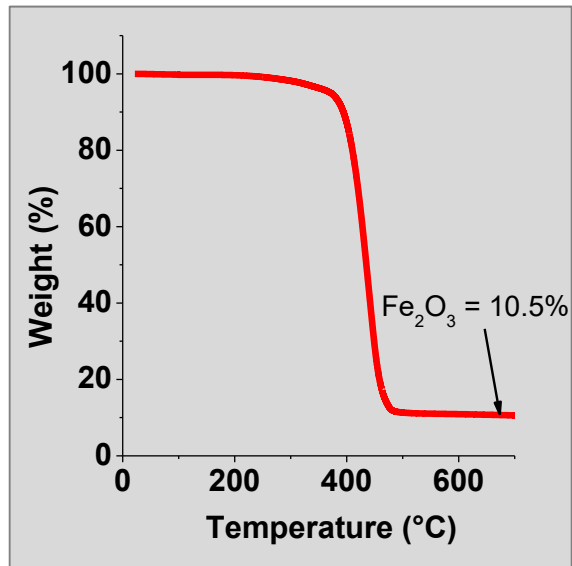
SPION polymer nanorattles (SEM)



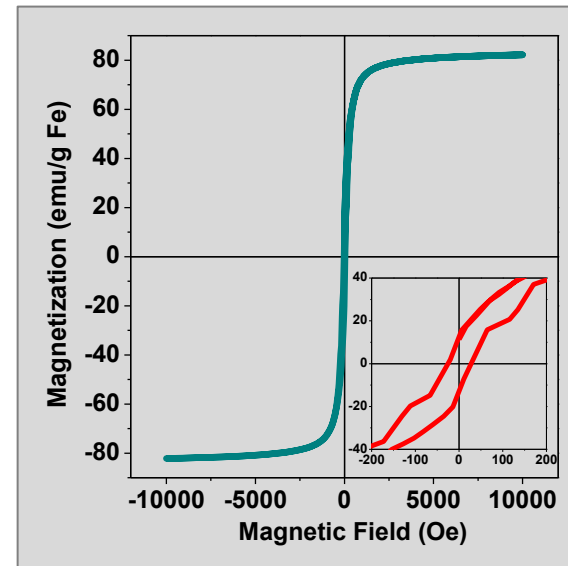
- Still maintain shell integrity: no broken shells

SPION nanorattles – TGA and magnetism

TGA: $\text{Fe}_2\text{O}_3 = 10.5\%$



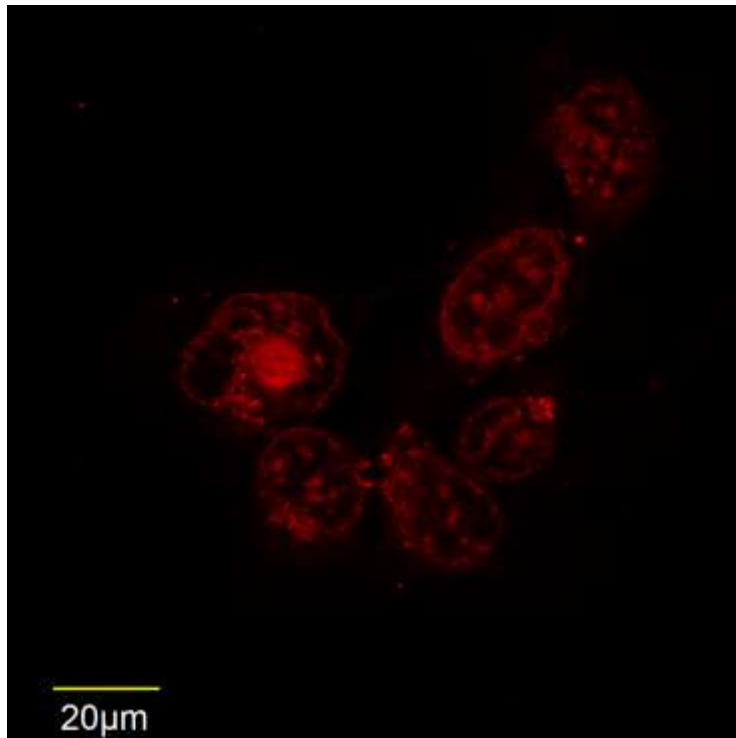
M_s 80 emu/g Fe



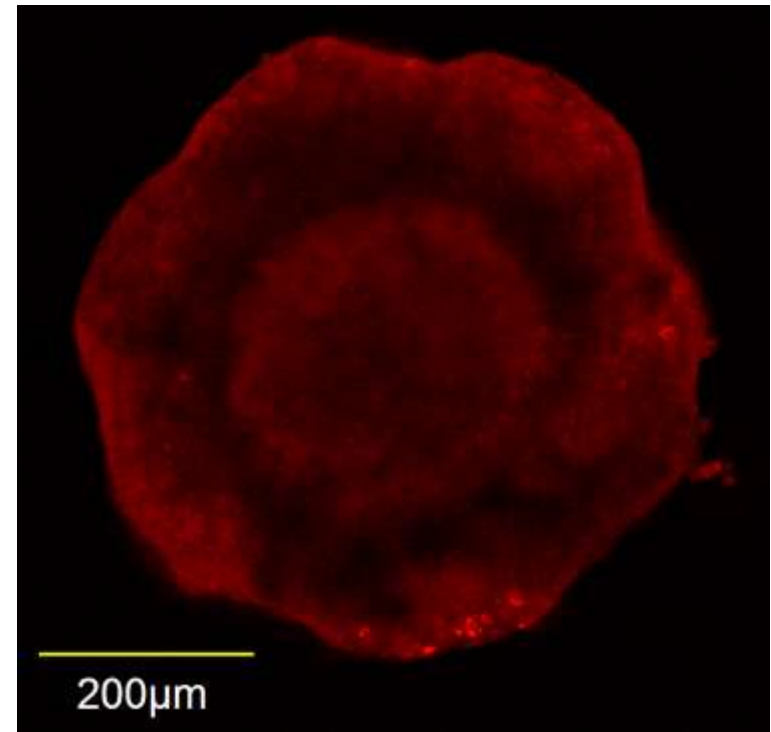
- Contain mostly polymer (89.5wt.%)
- Maintain superparamagnetic property of the original SPIONs

Dr Nguyen Pham: Penetration of Doxorubicine loaded nanorattles into 2D DLD-1 cancer cells and 3D DLD-1 spheroid

DLD-1 monolayer dosed with Dox-NRs (1uM as Dox) for 24h



DLD-1 spheroids were dosed with Dox-NRs (1uM as Dox) for 48h



Conclusions

- Iron oxide polymer nanorattle synthesis by polymer encapsulation of pigment using RAFT
- 185 nm in size with 50-100 nm voids containing SPIONs
- Monodisperse and superparamagnetic
- Doxorubicine loaded nanorattles could be taken up by cancer cells and penetrate 3D spheroid

Acknowledgments

- A. Professor Brian Hawkett, Prof. Chiara Neto, Prof. Greg Warr
- DuluxGroup Australia and their team: Dr Tim Davey, Dr Olga Paravagna, Dr Priya Subramanian, Dr Ewan Sprong
- Dr Nguyen Pham, Dr Thu Lam, Dr Vien Huynh
- Sirtex and Dr Steve Jones
- ARC
- ACMM
- KCPC members