Characterisation of Core@Shell Nanoparticles using Advanced Electron Microscopy

Andrew Wheatley
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Magnetic Core@Shell Nanoparticles

- Dual functionality
- Oxidative Stability
- Functionalisable
- Tuneable
- Recoverable
- Inexpensive

Catalytically active
Magnetic
Low Cost
Oxidatively stable

Applications in
- Magnetic separation
- Catalysis
- Drug delivery
- Magnetic hyperthermia
Synthesis of core@shell particles

- Sequential reduction/decomposition
  \[ A \xrightarrow{\text{Heat}} \text{Core@shell} + B \xrightarrow{\text{Heat}} \text{Core@shell} \]

- Simultaneous reduction/decomposition
  \[ A + B \xrightarrow{\text{Heat}} \text{Core@shell} \]

- Segregated mixture (alloyed)
  \[ \text{Core@shell} \]
  \[ \text{Heterodimer} \]
  \[ \text{Segregated mixture} \]
  \[ \text{Intermixed (alloyed)} \]
Characterisation of heterostructures

- **Powder XRD**
  - Can identify phases present
  - Sherrer equation gives particle size
  - Bulk technique
  - Peaks broadened by small crystallites
  - Size information only relevant to the smallest particles
  - Particles may be polycrystalline

- **Bright-field TEM**
  - Particle forms directly observed
  - Lattice fringes give information on phase
  - Core@shell structure may be visible
  - Increase in particle size could be caused by aggregation
  - Beam damage can occur
  - Core@shell structure may not be visible
  - Suffers from lens abberations

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Characterisation of heterostructures

• High-angle annular dark-field (HAADF) STEM
  ▪ Z-contrast is high
  ▪ Poor signal-to-noise ratio
  ▪ Reduced image resolution

• Spatially resolved EDS and EELS
  ▪ Produces elemental line scans
  ▪ Maps individual particles
  ▪ EDX best for high Z, EELS best for low Z

• Energy Filtered (EF) TEM
  ▪ Electrons with a particular energy loss are selected
  ▪ Selection based on core losses for specific elements
  ▪ Composite images for element mapping
  ▪ Poor signal-to-noise ratio

• Electron diffraction and fast Fourier Transforms
  ▪ Requires less material than XRD
  ▪ Bulk technique
  ▪ Suffers from lens aberrations

http://www-hrem.msm.cam.ac.uk/research/EFTEM/EFTEM.html
Synthesis of core@shell particles

1. PPh$_3$, 2) OA, 1) ex. Fe(CO)$_5$, 120 ºC, 2) 180 ºC, 3) 250 ºC

OA = cis-Me(CH$_2$)$_7$CH=CH(CH$_2$)$_7$CO$_2$H

HRTEM analysis of the product

- Mean particle size = 13.6 ± 1.2 nm
- Core@shell structure clear
- Inner shell and outer shell?
- Background of small (<2 nm) particles
High Resolution TEM

- Metallic Co core
- Partial oxidation in the shell
- Polycrystalline shell
Comparing bulk and individual particle analysis

- SAED and FFT combine bulk and individual particle analysis
- Metallic Co core
- Partially oxidised shell
Reconstructing particle images

- Inverse-FFT regenerates the particle image from the diffraction pattern
Elemental characterisation by line scans
Confirming the oxidation states – EELS line scans

- EELS data obtained for the L\textsubscript{2,3} edge of Fe
- 95 particles scanned
- Calibrated with respect to the Co L\textsubscript{2} edge
- Comparison of data from shell, ‘core’ and reference materials confirms that shell is closest in nature to Fe\textsubscript{3}O\textsubscript{4}
Verifying the location of carbon – EELS point scans

- Fe-rich background (2 nm particles)
- $\text{Fe}_3\text{O}_4$ shell must act to retain both C and Co
Conclusions and further work

• Core@shell@shell structure and metal oxidation states established

• Monocrystalline Co core, polycrystalline Fe₃O₄ outer-shell – formed by agglomeration of background Fe₃O₄?

• Presence of C inner-shell confirmed
  • Possibility of lowering epitaxial constraints at the core-shell interface
  • C may help protect the Co core

• Vary core size/material, outer-shell thickness, and capping to tune stability and properties
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