Electron Microscopy

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Outline

1) Introduction

2) Background to Electron Microscopy

3) TEM - Transmission Electron Microscopy
   including: Electron Diffraction
   HREM - High Resolution Electron Microscopy
   EDX - Energy Dispersive X-ray Spectroscopy

4) STEM - Scanning Transmission Electron Microscopy
   including: HAADF - High Angle Annular Dark Field Imaging
   EELS - Electron Energy Loss Spectroscopy

5) Examples

6) Conclusions
6) Examples

A transmission electron microscopy study of Fe-Co alloy nanoparticles in silica aerogel matrix using HREM, EDX, and EELS

A. Falqui, A. Corrias, M. Gass, and G. Mountjoy

10wt% Fe-Co alloy nanoparticles dispersed in silica aerogel matrix

two samples: (i) $\text{Fe}_{0.5}\text{Co}_{0.5}$ composition
(ii) $\text{Fe}_{0.67}\text{Co}_{0.33}$ composition
X-ray diffraction pattern
* BCC diffraction peaks

(S)TEM bright field images

Fe\(_{0.5}\)Co\(_{0.5}\)

Fe\(_{0.67}\)Co\(_{0.33}\)

Diameter ~ 7nm
Diameter ~ 4nm
High Resolution Electron Microscopy obtained from TEM.
Energy Dispersive X-ray Spectroscopy

obtained with a 1.5nm probe positioned at the centre of a single nanoparticle

EDX composition $\text{Fe}_x\text{Co}_{1-x}$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Centre of Nanoparticles</th>
<th>Over the Whole Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}<em>{0.5}\text{Co}</em>{0.5}$</td>
<td>0.42 0.01</td>
<td>0.47 0.04</td>
</tr>
<tr>
<td>$\text{Fe}<em>{0.67}\text{Co}</em>{0.33}$</td>
<td>0.63 0.02</td>
<td>0.67 0.04</td>
</tr>
</tbody>
</table>
STEM High Angle Annular Dark Field Images

Electron Energy Loss Spectroscopy (obtained from 0.13nm probe)
STEM Energy filtered imaging

$\text{Fe}_{0.67}\text{Co}_{0.33}$
Fe\textsubscript{0.5}Co\textsubscript{0.5} alloy nanoparticles

SiO\textsubscript{2} aerogel matrix

EDX probe

EELS probe

4 nm pores
Study of CoFe$_2$O$_4$ nanoparticles in silica aerogel matrix

G. Mountjoy, A. Falqui, A. Corrias, M.F. Casula, D. Loche

- CoFe$_2$O$_4$ is a partially inverted spinel
- normal spinel: $A^{2+}[\text{Tet}](B^{3+2})[\text{Oct}]O_4$
- inverse spinel: $B^{3+}[\text{Tet}](A^{2+}B^{3+})[\text{Oct}]O_4$
- oxygen is located on a FCC lattice

CoFe$_2$O$_4$ nanoparticles dispersed in a silica aerogel matrix

two samples:  
(i) 10wt% CoFe$_2$O$_4$
(ii) 5wt% CoFe$_2$O$_4$

Thermal Remnant Magnetisation
(assume $K_{\text{bulk}}$)
10wt\% $\text{CoFe}_2\text{O}_4$ $d=6\text{nm}$
5wt\% $\text{CoFe}_2\text{O}_4$ $d=4\text{nm}$

X-ray Diffraction
(Scherrer equation)
10wt\% $\text{CoFe}_2\text{O}_4$ $d=6\text{nm}$

TEM scattering contrast images
(Image processing) 10wt\% $\text{CoFe}_2\text{O}_4$ $d=4-7\text{nm}$
High Resolution Electron Microscopy obtained from TEM

10wt% CoFe$_2$O$_4$

diffractograms from HREM image
High Resolution Electron Microscopy

10wt% $\text{CoFe}_2\text{O}_4$

obtained from STEM

Bright field

Annular Dark field
Figure 2: SuperSTEM bright field image of “needle” nanostructure in sample of 10wt% CoFe$_2$O$_4$ in SiO$_2$ heat treated at 900 C.
Multi-walled carbon nanotubes decorated with titanium nanoparticles: synthesis and characterization

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- synthesis multi-walled carbon nanotubes with 8mol% Ti
- material for H₂ storage (by adsorption onto Ti)
multi-walled carbon nanotubes (before Ti impregnation)

**SEM** secondary electron image

**TEM** bright field image
after Ti impregnation

**TEM** bright field images and **electron diffraction** micrographs

**Figure 5.** (a) BF image of some MWCNTs. (b) BF image of a single MWCNT with dark spots corresponding to Ti nanoparticles. (c) SAED pattern from the MWCNT shown in (b). There are diffuse haloes due to the amorphous carbon film on the copper grid, and sharp rings due to the MWCNT.

**Figure 6.** A different single MWCNT with noticeable diffraction from the Ti-containing phase: (a) BF image, (b) DF image, (c) SAED pattern.
High Resolution Electron Microscopy obtained from TEM

**Figure 7.** HREM images: (a) MWCNT. (b) One particle of Ti-containing phase at the edge of a MWCNT. (c) Two particles of Ti-containing phase outside MWCNT.
Electron energy loss spectroscopy obtained from TEM

Ti L_{2,3} edges

**Figure 8.** EELS spectra of Ti L\textsubscript{3}- and L\textsubscript{2}-edges in: (a) Ti-decorated MWCNTs, (b) Ti metal [22], (c) TiO\textsubscript{2} anatase [22] (the rutile spectrum is very similar).

O K edge

**Figure 9.** EELS spectra of O K-edge in: (a) Ti-decorated MWCNTs, (b) TiO\textsubscript{2} anatase [23] (the rutile spectrum is very similar).
Study of FePt:CdS nanoparticles

- special synthesis of FePt:CdS nanoparticles
- to create magnetic particles with semiconductor label
- as prepared particles are core-shell
  - core of FePt
  - shell of CdS
- heat treatment cause "de-wetting" of shell to create dimer
FePt:CdS core-shell nanoparticles

TEM/STEM bright field images

High resolution electron microscopy obtained from TEM/STEM
FePt:CdS dimer nanoparticles

TEM/STEM bright field images

High resolution electron microscopy obtained from TEM/STEM
Conclusions

- TEM is a versatile instrument but requires special training to operate
- TEM with scattering contrast and electron diffraction can identify phases within microstructure
- TEM / STEM or dedicated STEM can identify composition on nm-scale
- TEM is an essential instrument for structural characterisation
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