

CONTROL OF PHASE OF IRON OXIDE

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Outline

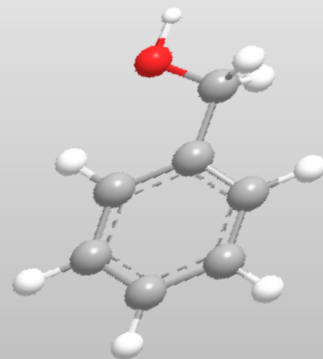
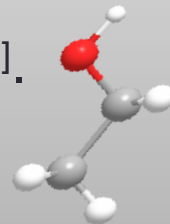
- Phases of Iron Oxide
- Common Synthesis Methods
- Experimental
- Characterization
- Future Work

Phases of Iron Oxide

- Three primary oxidation states of Iron Oxide
- Iron(II) oxide
 - Wüstite - FeO
- Iron (III) oxide
 - Hematite - $\alpha\text{-Fe}_2\text{O}_3$
 - Maghemite - $\gamma\text{-Fe}_2\text{O}_3$
- Iron (II,III) oxide
 - Magnetite - Fe_3O_4
- Iron Oxide has a number of applications
 - Magnetic properties
 - Photocatalysis
 - Energy applications

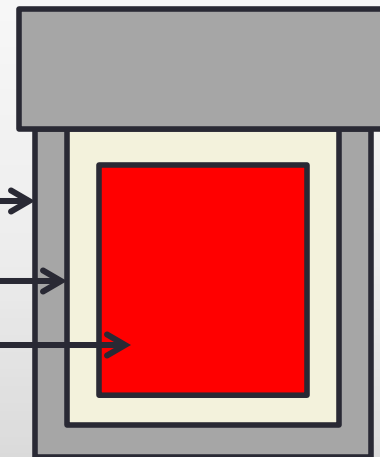
Common Synthesis of Iron Oxides

- Early methods employ aqueous co-precipitation methods
 - pH > 11
 - Metal halide salt precursor
 - Surfactants to control size and morphology
- Pinna *et al.* (2005) developed a surfactant free one step solvothermal synthesis of Fe_3O_4 & $\gamma\text{-Fe}_2\text{O}_3$ ^[1].
 - Iron(III)Acetylacetonate and benzyl alcohol
- Qian *et al.* (2012) hybridized Fe_3O_4 on graphene^[2].
 - Iron(III)Acetylacetonate and ethanol



Solvothermal Synthesis

- Method of nanoparticle production
 - Stainless steel autoclave
 - Teflon liner
 - Solvent/Precursor solution
- Creates internal pressure within the autoclave
 - Pressure arises solely from heating solvent past the boiling point
- Variables of solvothermal synthesis
 - Temperature
 - Solvent/precursor solution
 - Synthesis time

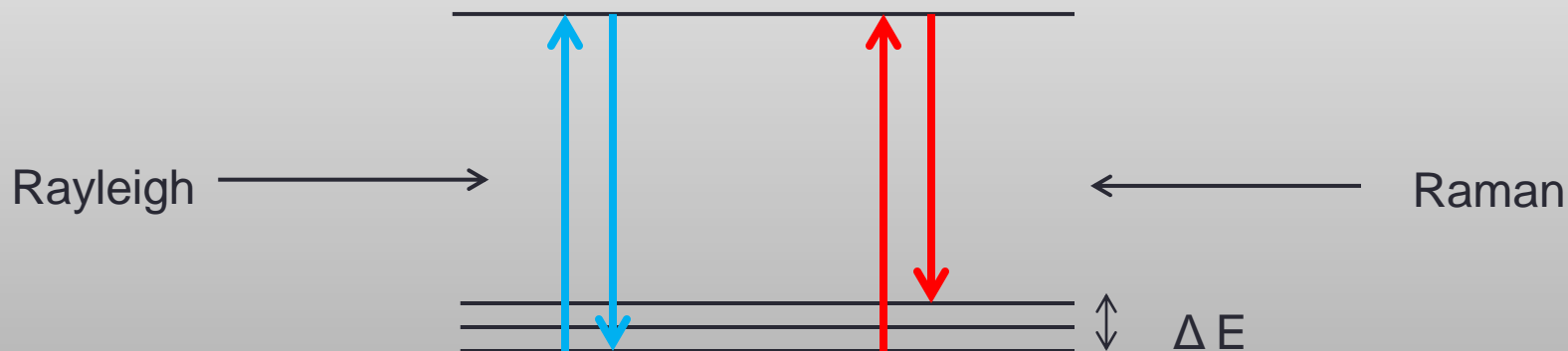


Preparation of Nanoparticles

- 5 mM solution of $\text{Fe}(\text{Acac})_3$ and solvent (ethanol or acetone)
- 1 mg of few layer graphene
- Mixture transferred to a Teflon liner and stainless steel autoclave
- Heated for 24 hours at varied temperatures
 - 70°C & 180°C
- Precipitate centrifuged at 14800 rpm for 15 minutes

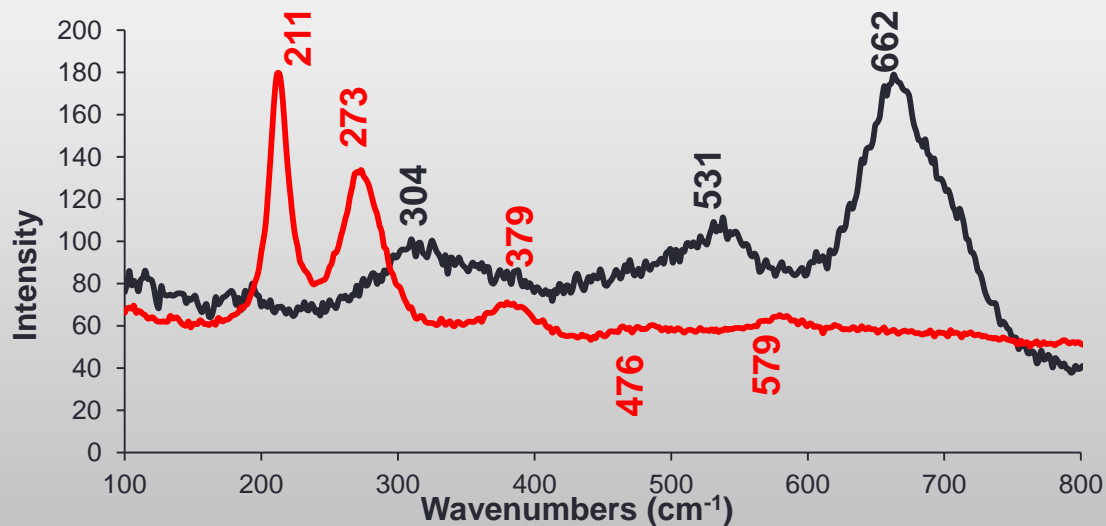
Raman Spectroscopy

- Raman is a scattering spectroscopy arising from a change in polarizability of a molecule
- Generally light scattering is elastic
 - Rayleigh scattering- no change in energy and frequency
- A small amount of light will result in inelastic scattering
 - Raman scattering- change in energy and frequency

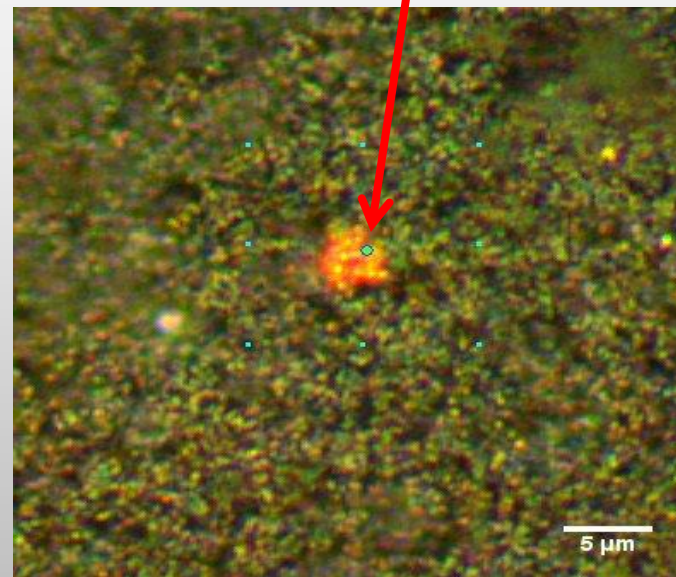


Effect of Laser on Fe_3O_4

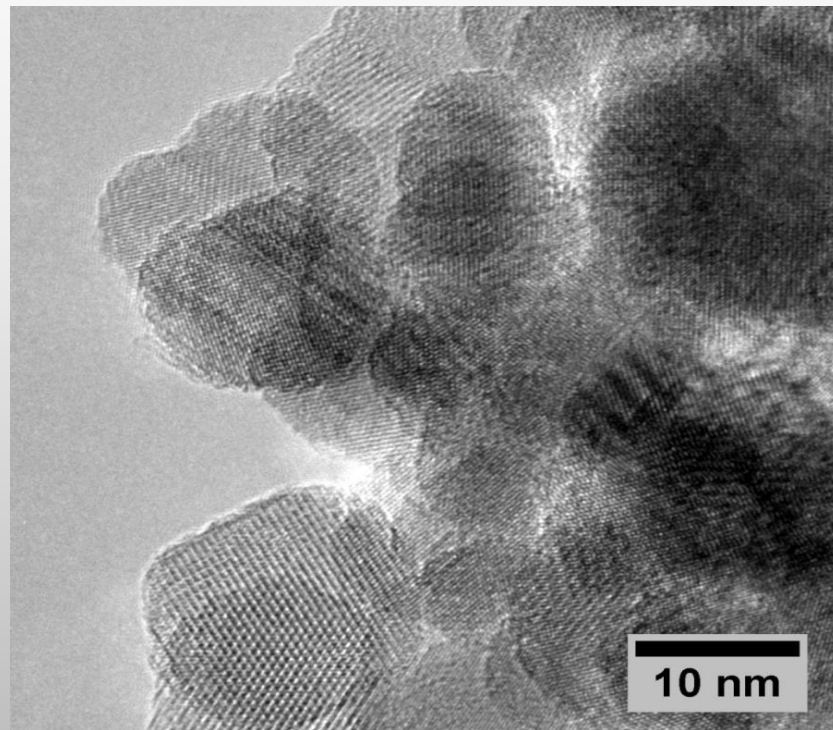
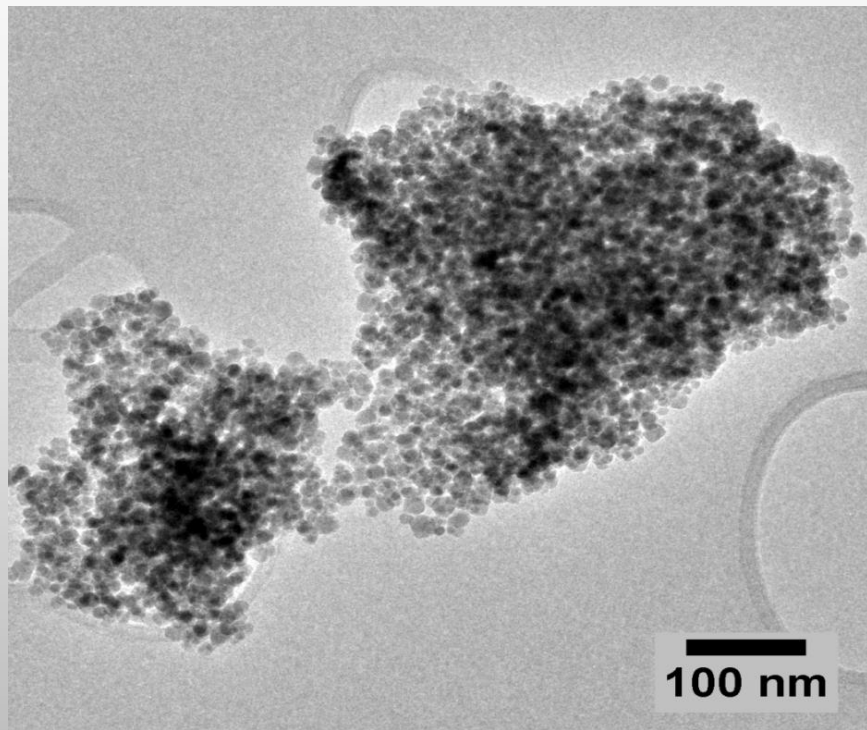
Raman laser power < 1 mW,
Raman laser power > 1 mW



Area exposed to laser

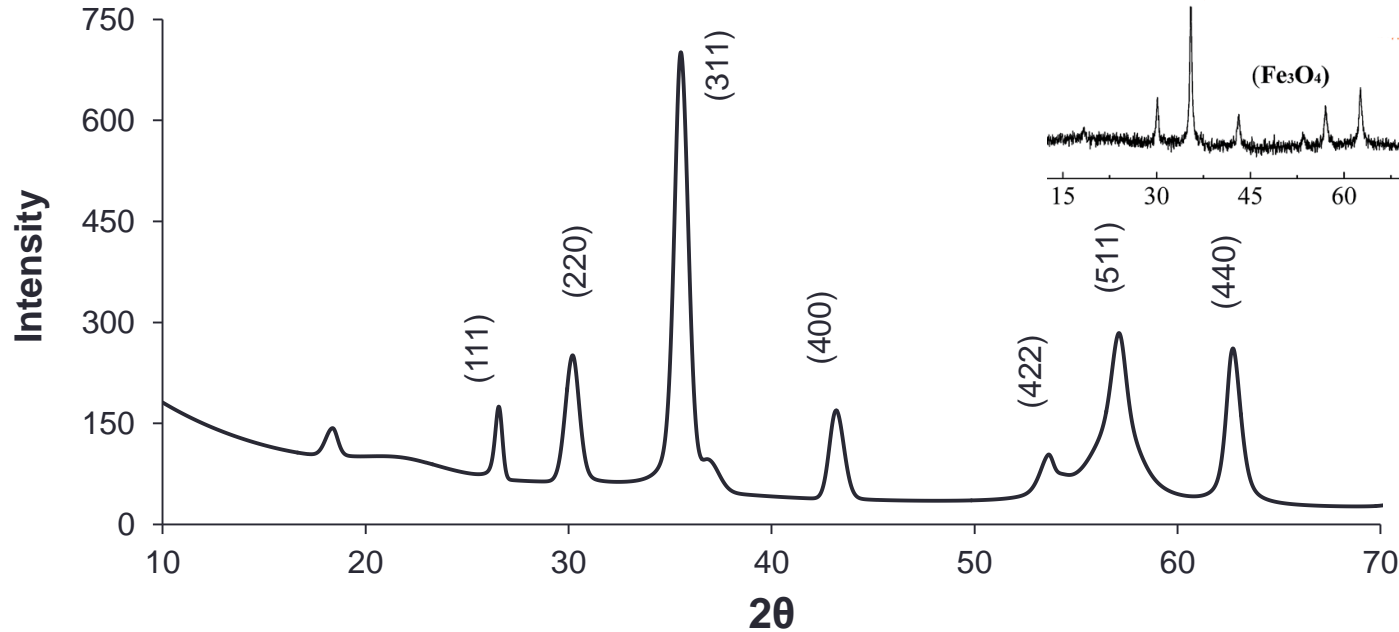


TEM Fe_3O_4



TEM of nanoparticles, reaction in ethanol at 180°C for 24 hours

X-Ray Diffraction of Iron Oxide

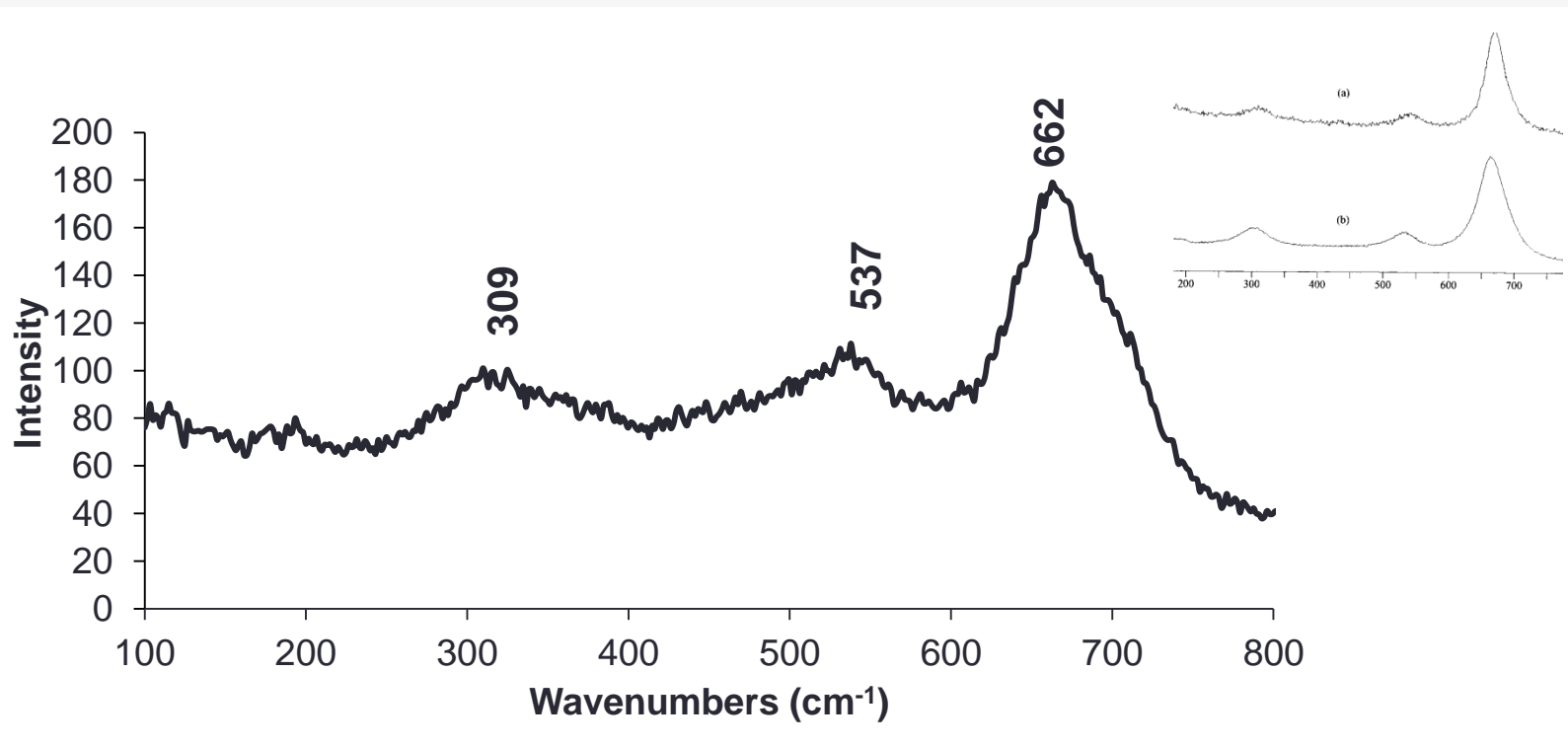


• θ

- 26.5° (111)
- 30.1° (220)
- 35.5° (311)
- 43.0° (422)
- 53.3° (511)
- 57.0° (511)
- 62.6° (440)

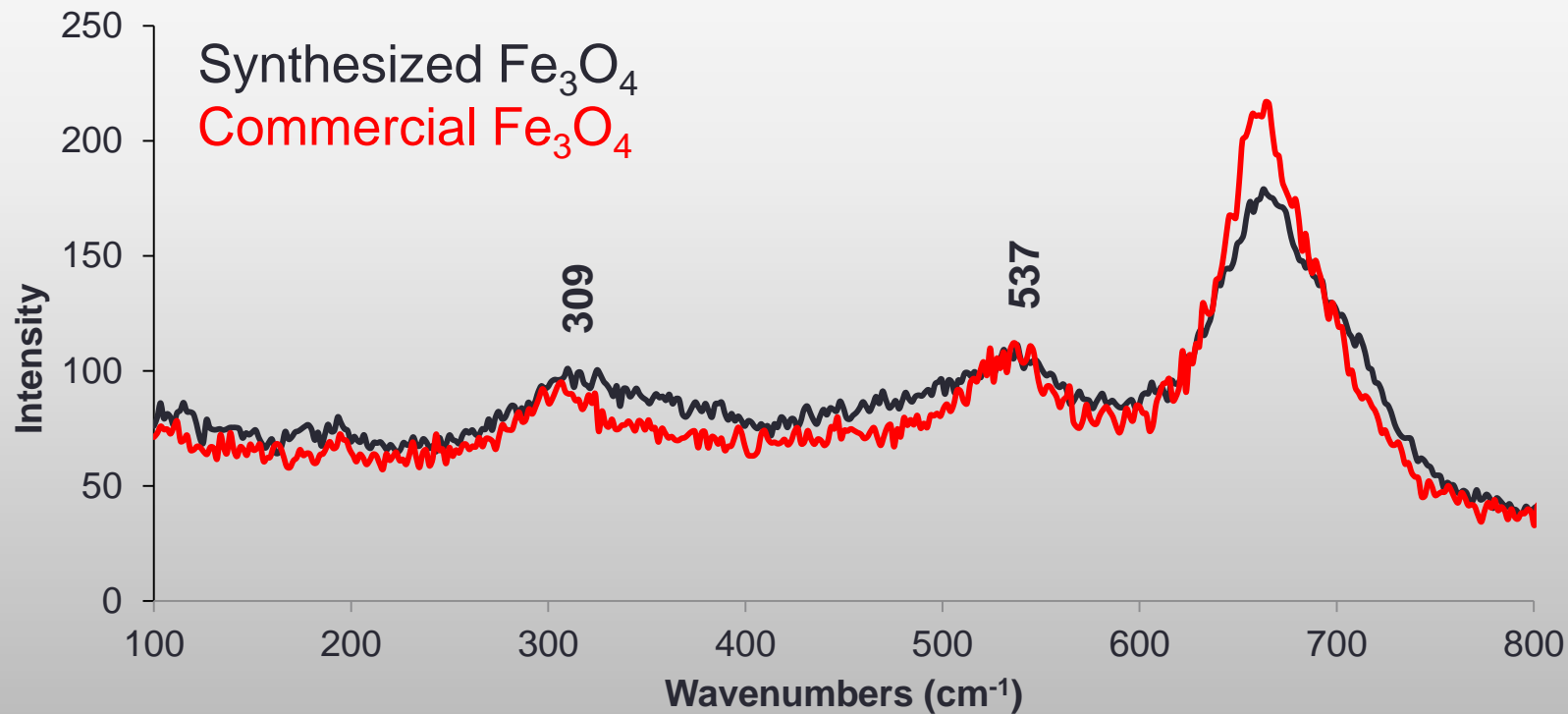
XRD spectra characteristic of the spinel structure^[3]

Ethanol Reaction at 180°C

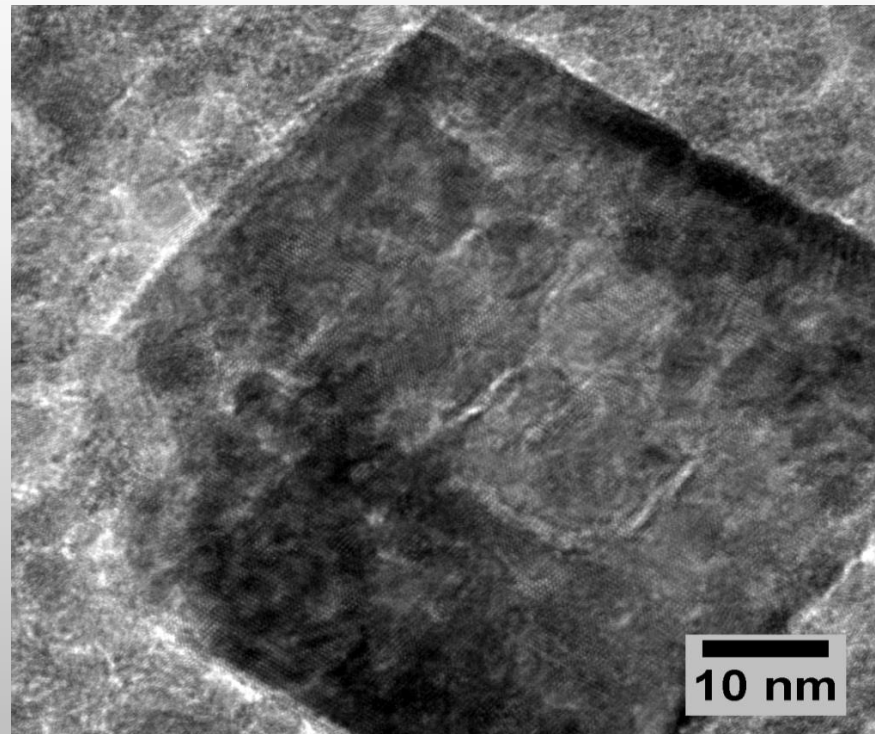
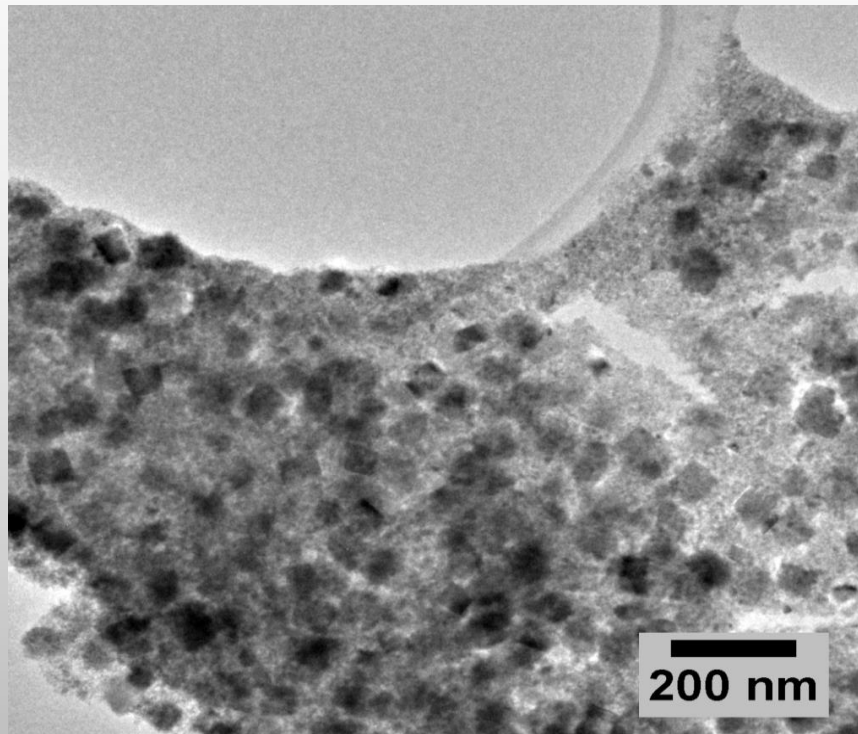


Raman spectra characteristic of Fe₃O₄^[4]

Commercial vs. Synthesized

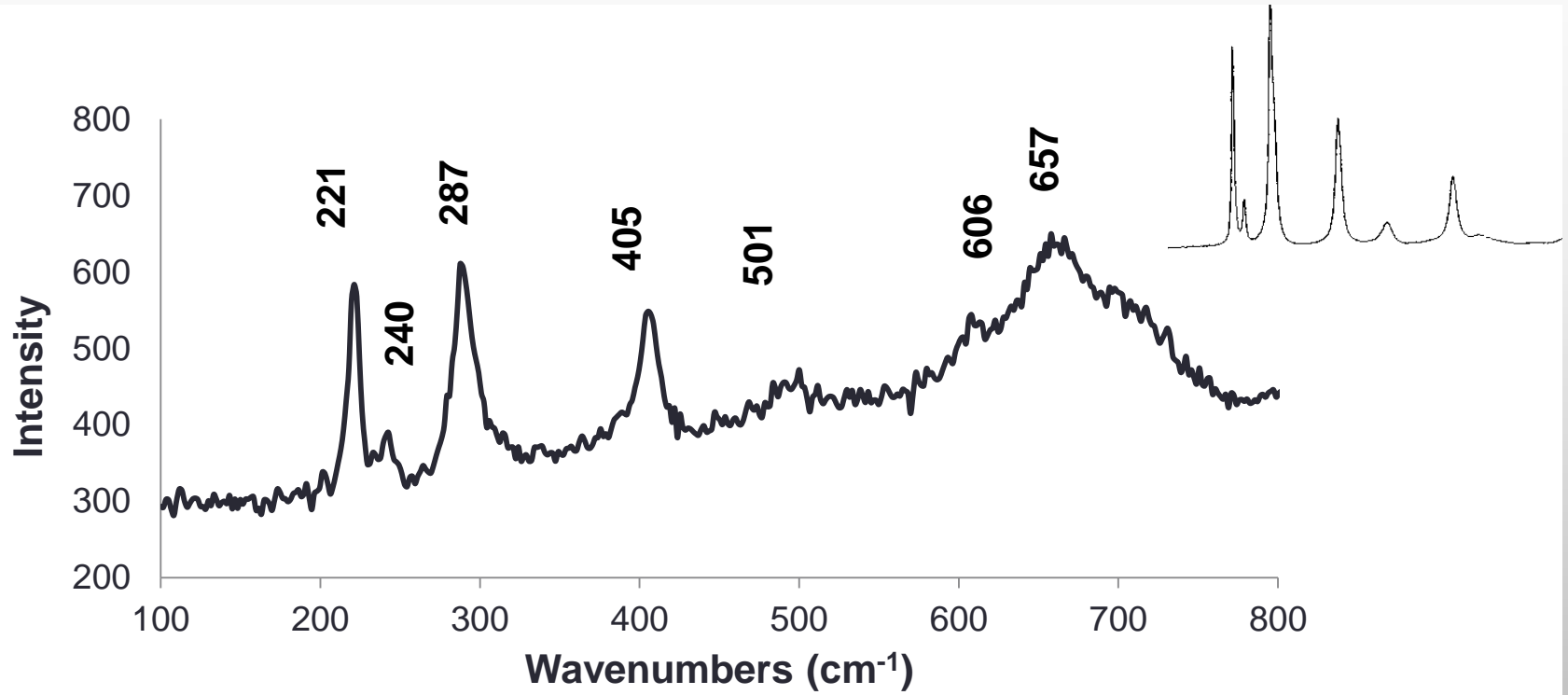


TEM α -Fe₂O₃



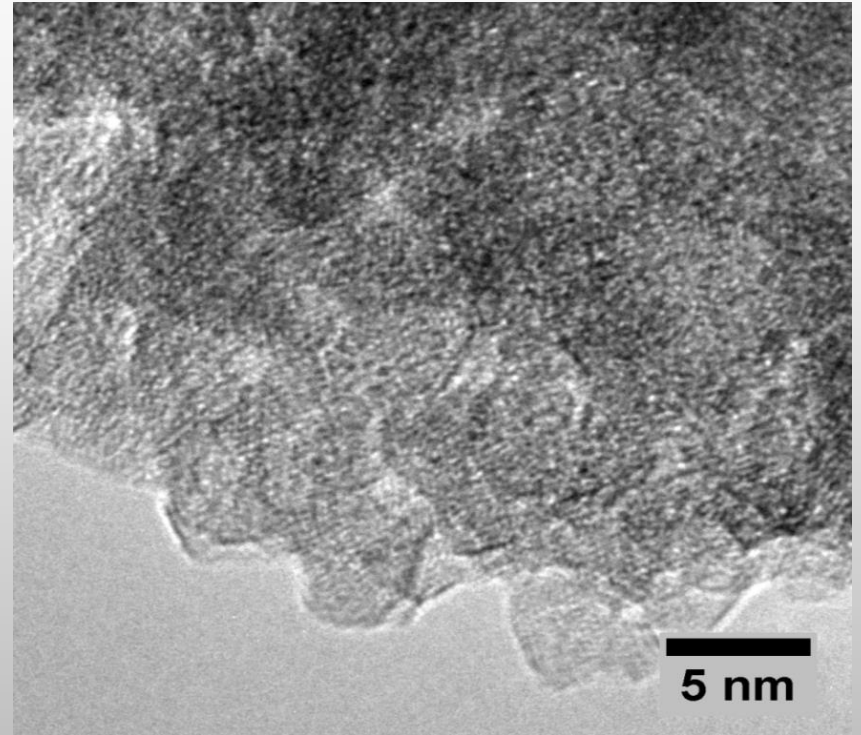
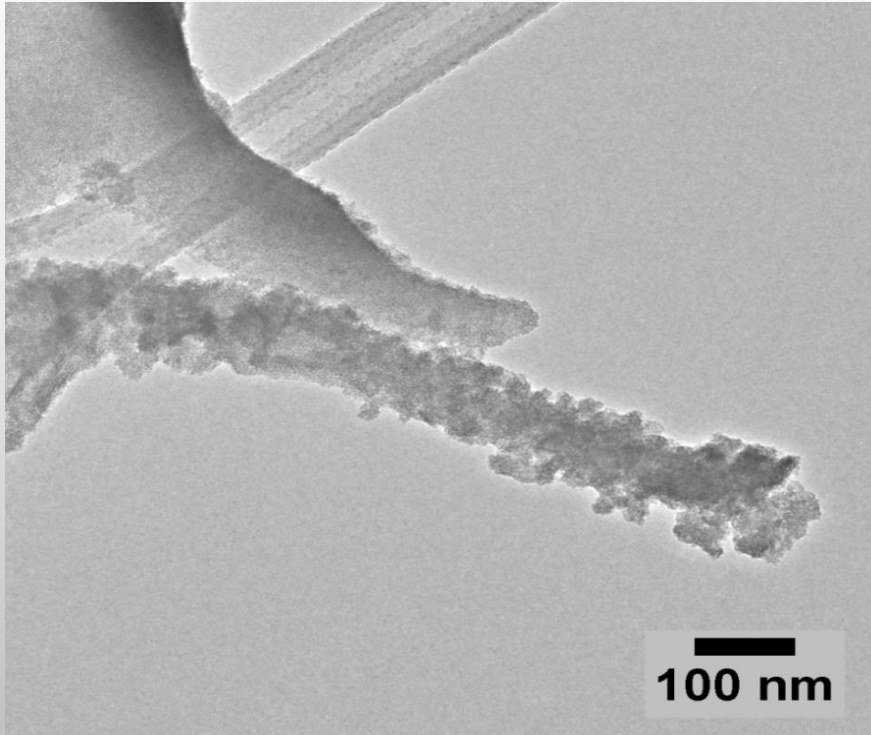
TEM of nanoparticles, reaction in acetone at 180°C for 24 hours

Acetone reaction at 180°C



Raman spectra characteristic of $\alpha\text{-Fe}_2\text{O}_3$ ^[4]

TEM α -Fe₂O₃



- TEM of nanoparticles, reaction in acetone at 70°C for 24 hours

Future Work

- Obtain XRD spectrum of $\alpha\text{-Fe}_2\text{O}_3$
- Extend reaction time of acetone solvothermal to 48 hours
- $>200^\circ\text{C}$ temperature synthesis in both solvents

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Citations

1. N. Pinna, G. Garnweitner, M. Antonietti, and M. Niederberger, "A General Nonaqueous Route to Binary Metal Oxide Nanocrystals Involving a C–C Bond Cleavage," *J. Am. Chem. Soc.*, vol. 127, no. 15, pp. 5608–5612, Apr. 2005.
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