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Ionic liquid synthesis of metal oxide nanoparticles for energy generation and green chemistry



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1. Context

Many **metal oxides**, particularly spinel ferrites, have **promising electronic structures** that suggest applications in photocatalysis¹ or photovoltaics. To retain these atomic properties in the bulk quantities required for devices, we need to **control the crystalline phase** as well as the elemental composition of the oxide.

Particle size is also important: efficiency can be expected to go up as the particle size decreases and a larger surface area is available to react.

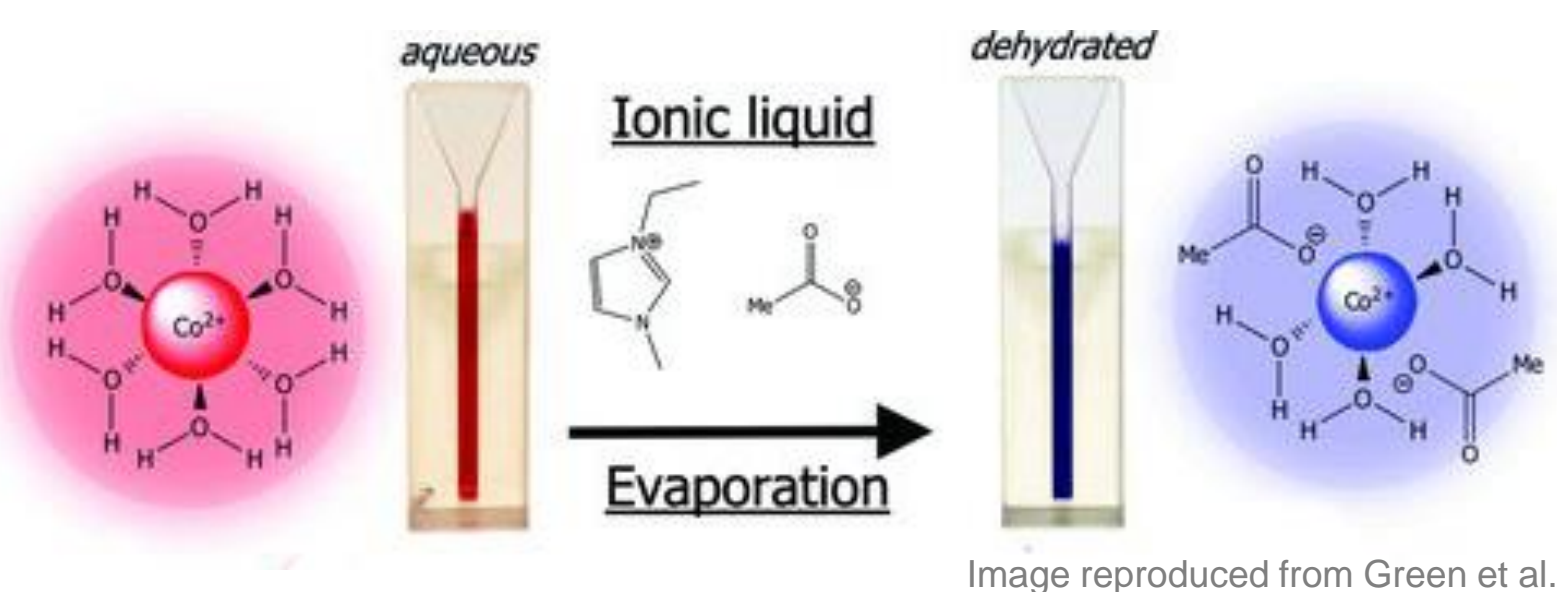
Ionic liquid synthesis has successfully been used to generate phase-pure crystallites of complex oxides: could it work here?

Target: Copper ferrite, CuFe_2O_4

- Band gap tunable between 1.2-1.4 eV²
- Spinel structure
- Multiple uses
- Earth-abundant
- Low toxicity
- Magnetic: recoverable

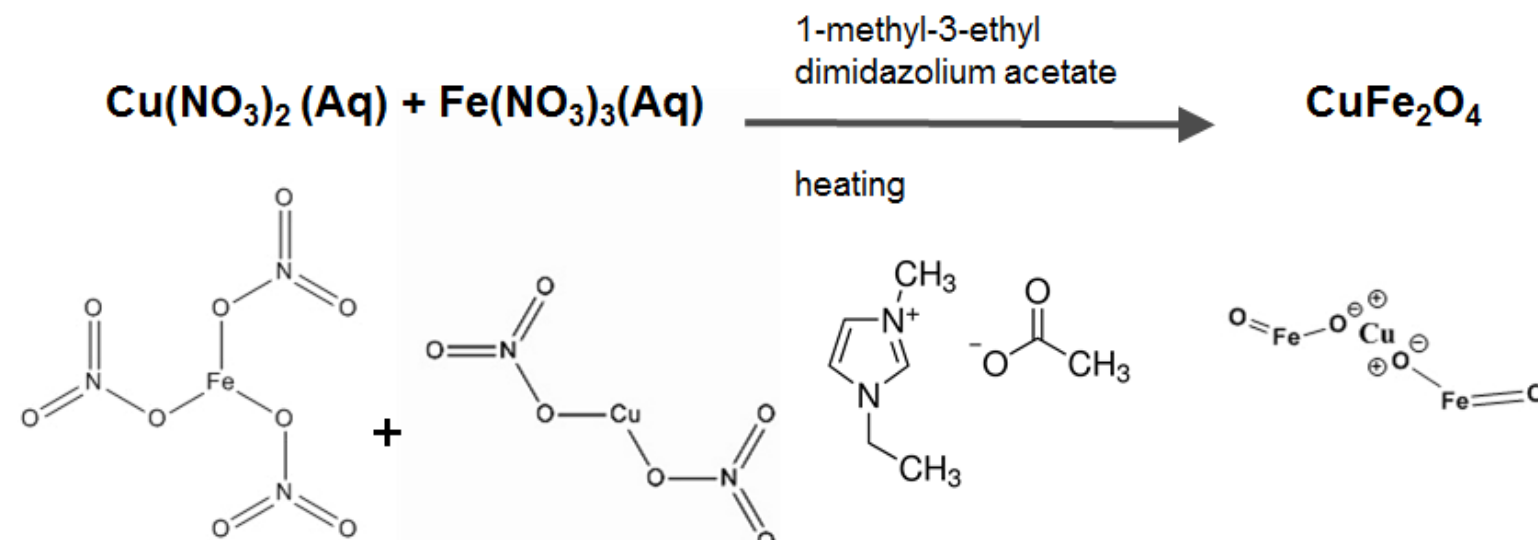
2. Materials and methods

Ionic liquid synthesis³



Ionic liquid (IL) synthesis can produce phase-pure oxides from even poorly solvating metal ions, and control morphology of growing crystallites. The technique ensures complete sequestration of reactants and promotes even distribution during heating and oxidation. Additional coordination may be provided by biotemplates such as cellulose or dextran. The synthesis is one-pot and operates in ambient conditions, and has been used to create complex quinary superconductors in customised morphologies.

Reaction scheme



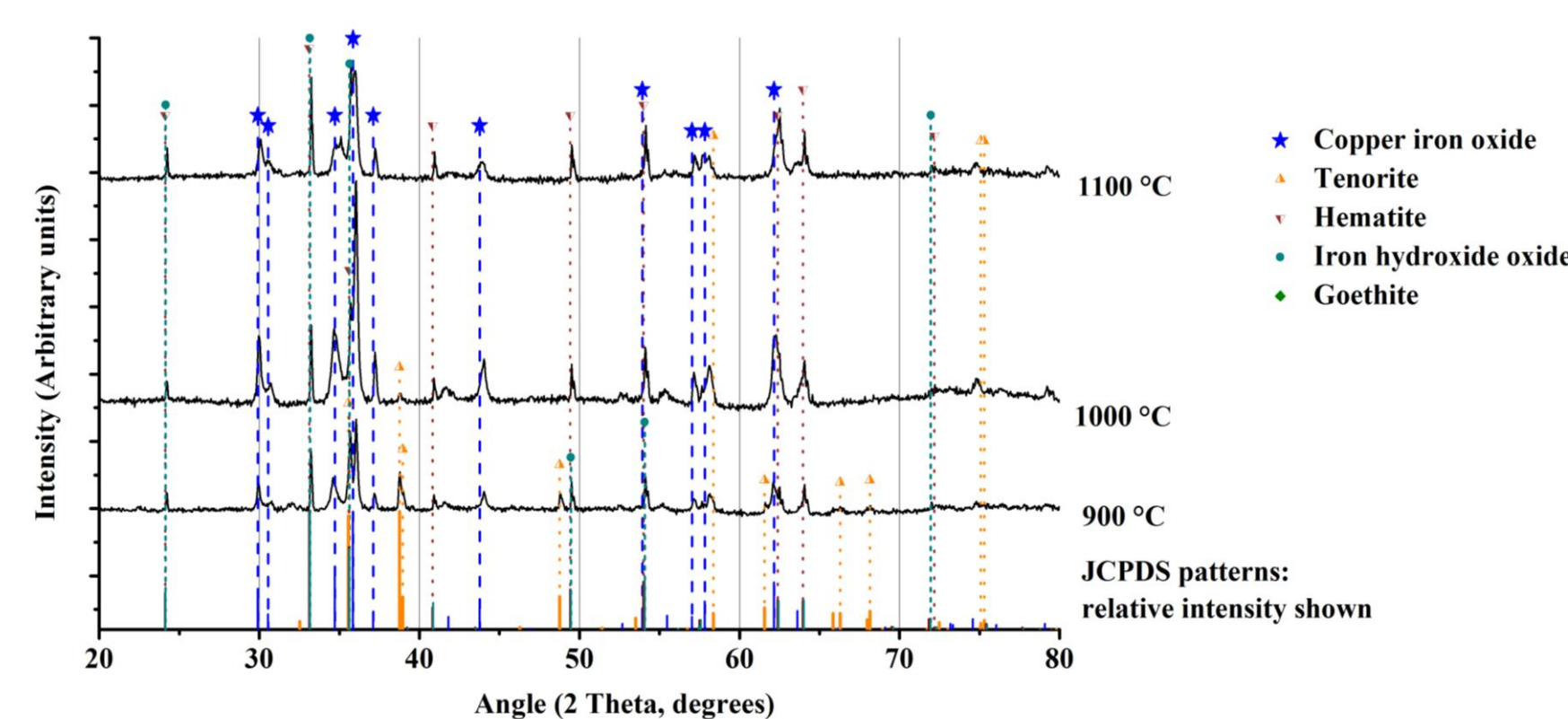
Variables:

- Temperature
- Time held at temperature
- Choice of metal precursors
- Concentration of precursors
- Choice of ionic liquid
- Addition of biotemplates

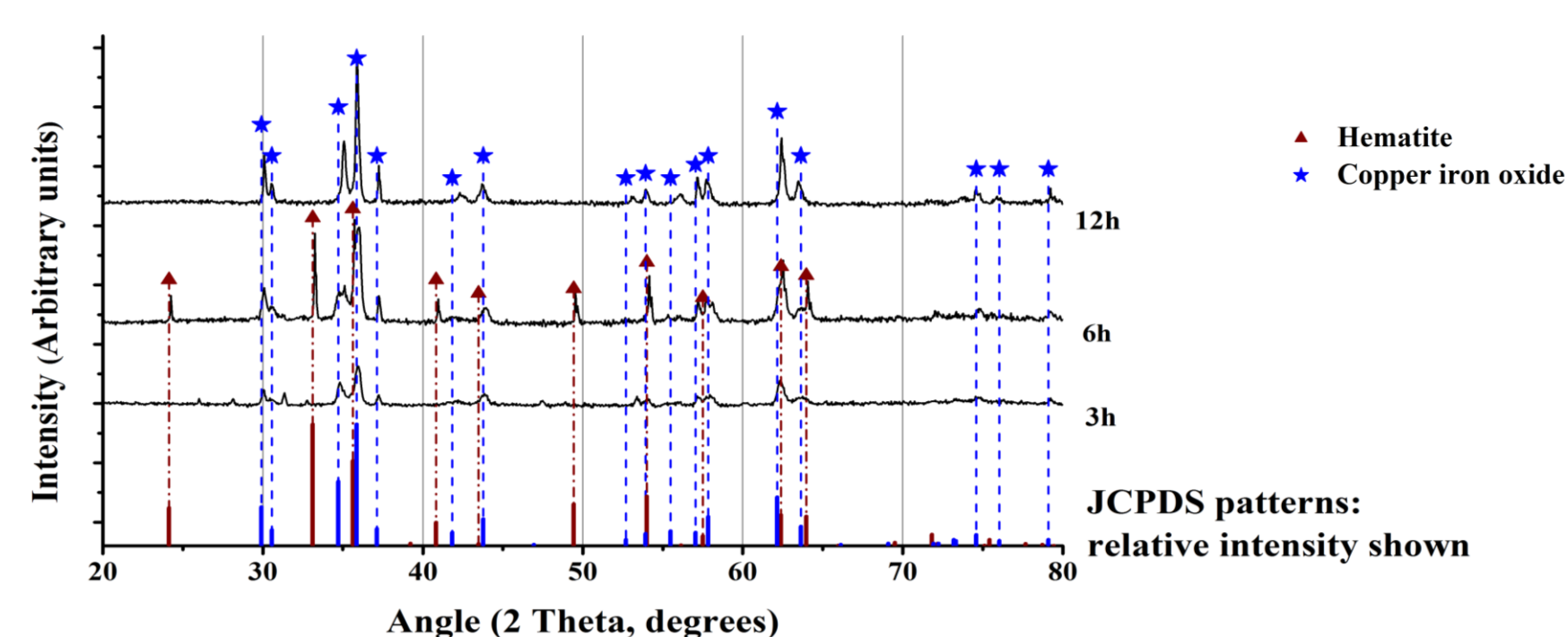
3. Results

X-ray Diffraction (XRD)

Results of varying temperature

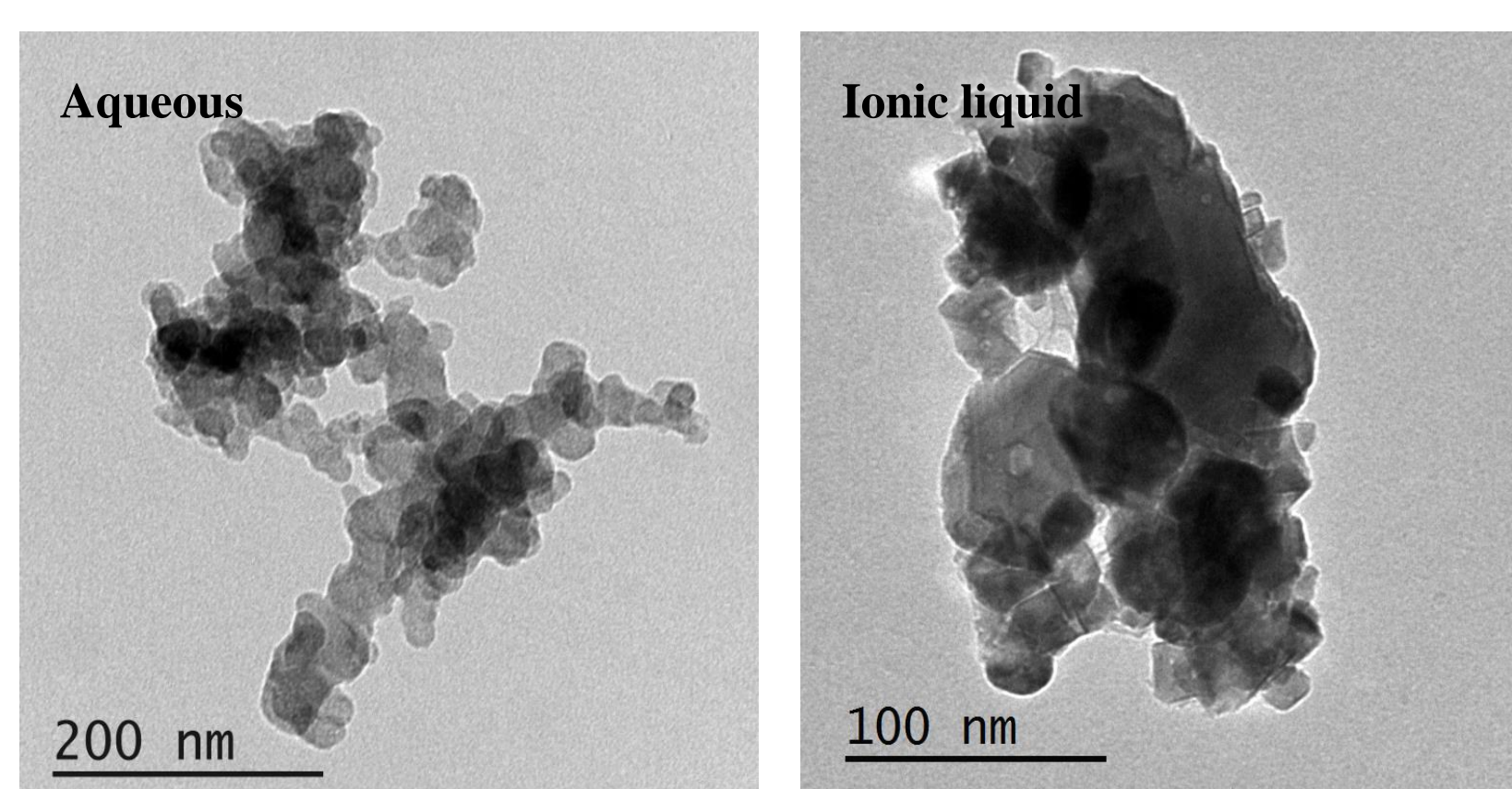


Results of varying hold time



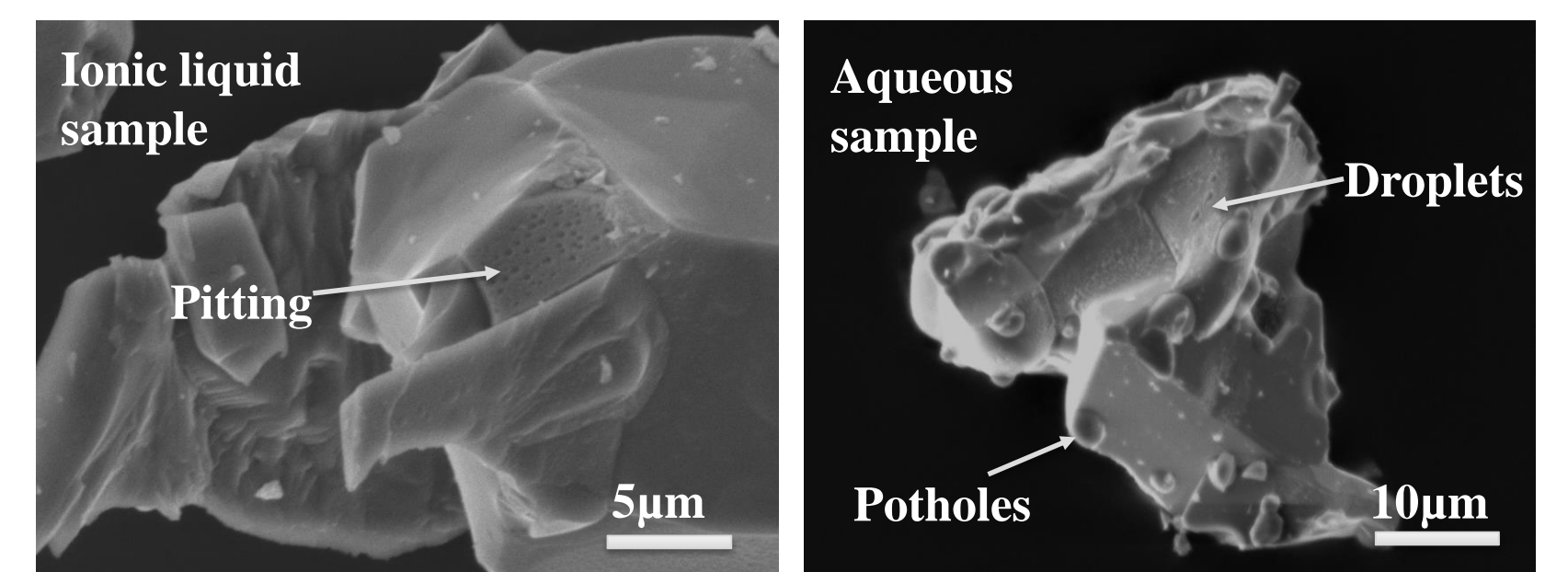
XRD studies demonstrated the disappearance of intermediate phases as hold time and temperature increased. At 1100 °C with a shorter hold time many phases were observed. When this is extended for 12 hours only the distorted tetragonal cuprospinel CuFe_2O_4 phase (JCPDS: 00-034-0425) remains. This was, surprisingly, true for both IL and aqueous synthesis, although only IL results are shown above.

Transmission Electron Microscopy (TEM)



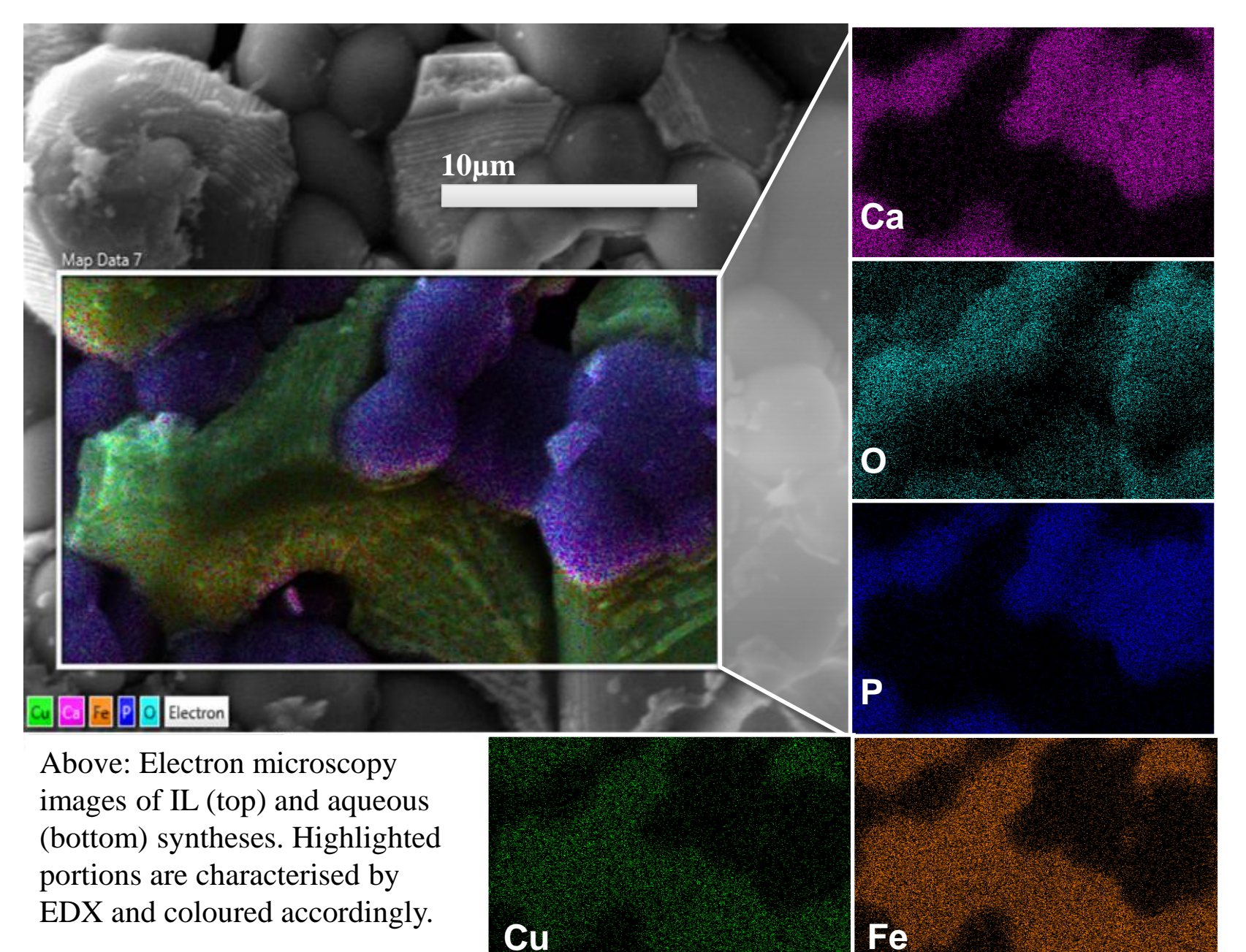
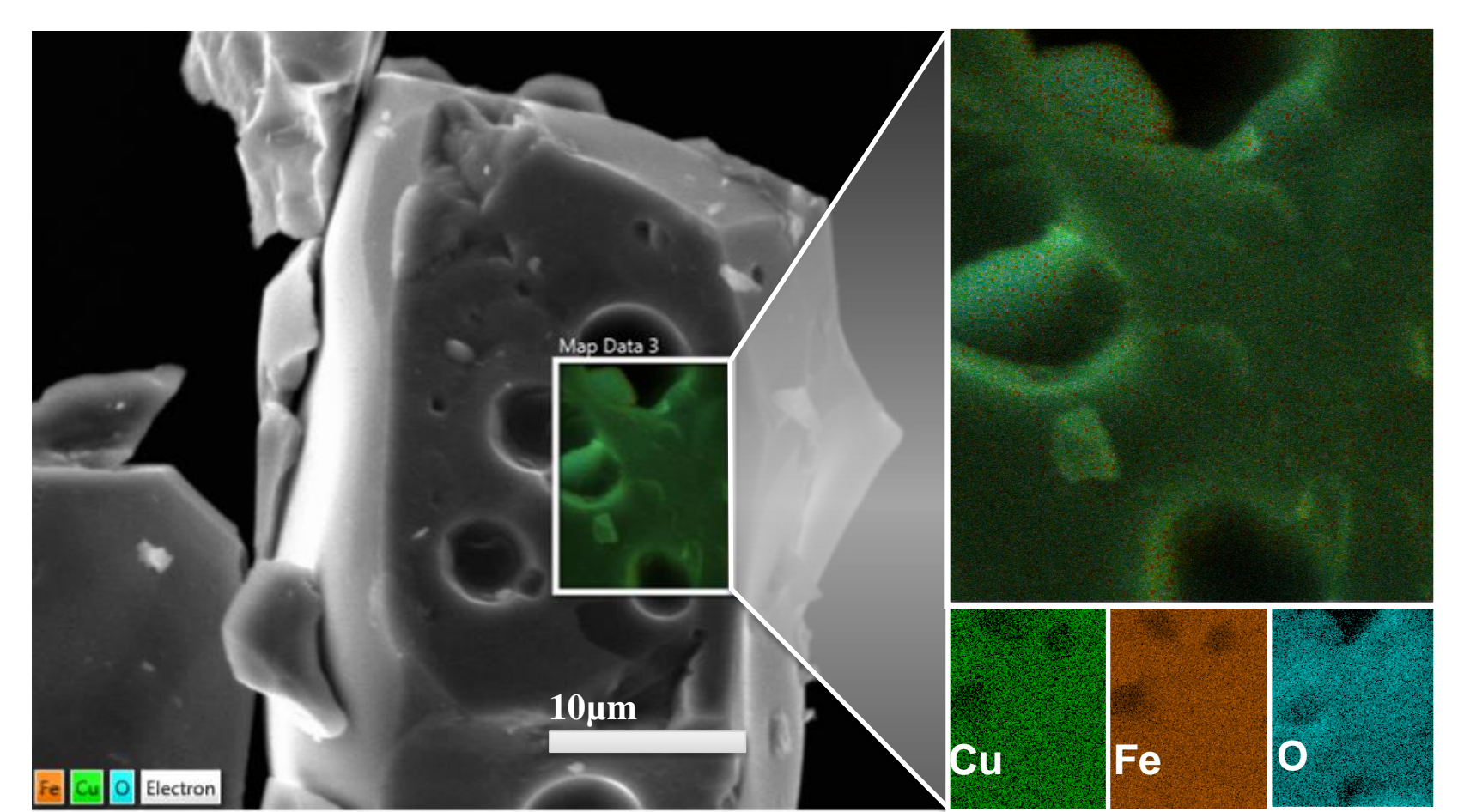
TEM identified nanoscale particles of copper ferrite in both synthesis. These were most commonly found aggregated, as shown here. All particles created were highly polydisperse and beam sensitive, making it challenging to image a representative sample. No consistent morphological differences between solvents were seen.

Scanning Electron Microscopy (SEM)



SEM images suggested at least some particles were nano-scale. Results of all syntheses, both those done in both aqueous and ionic liquid media and with or without biotemplating, exhibited surface features such as potholes, melted droplets and pitting. These were investigated further using elemental mapping.

Elemental Mapping



Above: Electron microscopy images of IL (top) and aqueous (bottom) syntheses. Highlighted portions are characterised by EDX and coloured accordingly.

Elemental mapping confirmed most surface features were CuFe_2O_4 , and identified the presence of amorphous calcium and phosphorus not seen in XRD. The source of these elements was unclear but suspected to arise from contamination of the deionized water.

4. Conclusions

IL synthesis was experimentally confirmed as an alternative route to **phase-pure spinel-phase CuFe_2O_4** . This required **temperatures of 1100 °C** and a **hold time of 12 hours**. A **polydisperse mixture** of nanoparticles was formed, which showed **the presence of calcium and phosphorus**. However, the majority of **surface features were confirmed as pure CuFe_2O_4** . Both ionic liquid and aqueous solution produced similar results, though ionic liquid yields were much higher.

Future work would explore approaching a monodisperse nanoparticle product at lower temperatures through the use of biotemplating, the addition of potassium and sodium ions, and alternative ionic liquids. Characterisation of the material's electronic and electrochemical properties will determine potential device applications.

References

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Acknowledgments

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