Towards the Continuous Production of Functional Nanomaterial Inks for 3D-Printed Electronic Device Applications Using Supercritical Water

R. Worsley,[a, *] **A. Bastola,**[b] **R. Hague,**[b] **C. Tuck,**[b] **E. Lester**[a]

[a]*Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK*

[b]*Centre for Additive Manufacturing, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK*

**Corresponding Author: robyn.worsley@nottingham.ac.uk*

1. Introduction

In the field of additive manufacturing, material jetting techniques are showing great promise for the scalable, digital fabrication of electronic devices.[1] The inherent capability of such techniques to selectively deposit and subsequently consolidate multiple functional materials within the same process enables structures of arbitrary complexity to be realized.[2] Electronic functionalities are often obtained through the use of nanomaterial-loaded solvent-based inks.[3] Conductive inks are widely available and produced on an industrial level, whilst more complex functionalities, such as magnetism and the piezoelectric effect, are difficult to obtain in printed features, with materials synthesised *via* traditional routes typically unsuitable for jetting.

Continuous hydro- and solvothermal production methods are capable of generating a wide variety of nanomaterials with tailorable electrical performances.[4] The products are suspended in solution and can be delivered at scale, with a high degree of control over particle characteristics, rendering this synthesis approach highly complementary to the fields of functional ink formulation and additively manufactured devices.

Barium titanate is a widely utilised ceramic material capable of exhibiting piezoelectric characteristics.[5] The continuous production of nanocrystalline barium titanate in supercritical water has already been demonstrated; however, these nanoscale particles exist mostly in the dielectric cubic perovskite phase,[6,7] whilst the tetragonal crystal phase is required for the exhibition of piezoelectricity. The tetragonal to cubic transition is dependent upon many factors, including the particle size, shape, surface chemistry, stoichiometry, and the influence of dopant atoms or defects.[8] Such factors exert a similar influence on the performance of magnetic nanoparticles, such as hexagonal ferrites,[9] determining their behaviour in response to an applied magnetic field.[10]

In this work, we explore the influence of varying synthesis parameters on the properties of barium titanate and barium hexaferrite nanoparticles obtained *via* a continuous hydrothermal method, with a view to achieving the optimal crystal structure for the fabrication of 3D-printed piezoelectric and magnetic devices.

2. Materials and Methods

Nanoparticle synthesis was performed *via* a counter-current nozzle reactor within a bench-scale continuous-flow system, designed at the University of Nottingham.[11,12]

For the synthesis of both barium titanate and barium hexaferrite nanoparticles, the appropriate water-soluble metal salt precursors were fed into the system at a concentration of ~0.05 M and a flow rate in the range of 5-10 mL min^{-1}, meeting a base mineralizer stream, fed at the same rate, in-flow and at room temperature. This combined 'cold' stream was then fed upwards into the nozzle reactor to meet a hot, pressurized flow of between 10-25 mL min^{-1} of supercritical water, leading to rapid nucleation of the nanoparticle product. The water was heated to a temperature between 350-430 °C and the pressure of the entire system was maintained at 240 bar. Parameters such as reaction temperature, precursor concentration, mineralizer concentration, residence time, flow ratios, and the use of supercritical solvent mixtures have been investigated, and their effects on product properties studied.

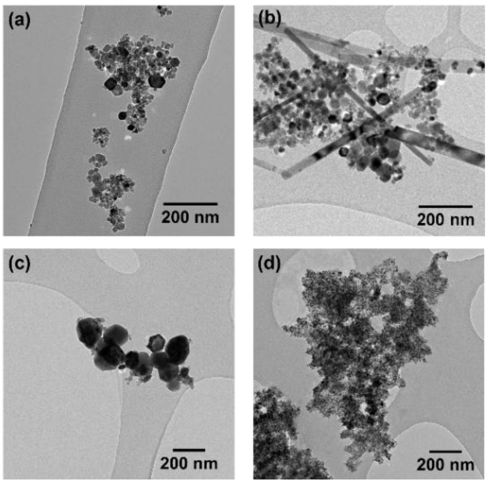

Figure 1. (a) Hydrothermally synthesised barium titanate nanoparticles and their modification through variation of the synthesis parameters, including (b) mineralizer concentration, (c) residence time, and (d) the use of supercritical solvent mixtures.

Particle size and morphology were characterized using transmission electron microscopy (TEM), whilst the phase and crystal structure were investigated *via* powder X-ray diffraction (XRD) and Raman spectroscopy.

Investigations have been made into surface functionalisation of the synthesised nanoparticles with organic dispersants, in order to aid ink formulation, stability for jetting, and improved performance in the final devices. Surface coverage has been measured using thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy.

3. Results and Discussion

Through variation of the supercritical synthesis parameters, barium titanate nanoparticles of differing size and shape have been obtained (Figure 1). Particle size strongly affects tetragonality, particularly at the nanoscale, as does the particle geometry, with high aspect ratio-materials predicted to retain tetragonality at very low diameters, in contrast to spherical particles.[6]

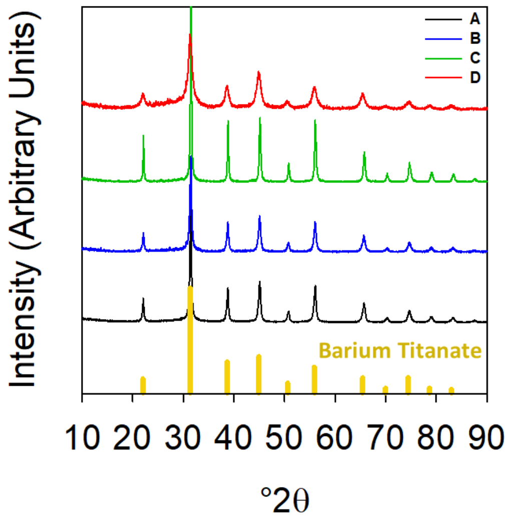

Figure 2. XRD patterns of barium titanate nanomaterials synthesised under differing supercritical fluid conditions.

Indeed, corresponding XRD data (Figure 2) for the materials shown in Figure 1 indicate differing degrees of tetragonality across the hydrothermal samples synthesised under differing conditions, as determined by the shape of the reflection at ~45° 2θ; this is further supported by complementary Raman spectroscopy data.

Similar results have been observed in barium hexaferrite experiments; the synthesis parameters greatly affect the material crystallization and subsequent magnetic properties.

FTIR data indicate an increased coverage of surface hydroxyl groups resulting from the supercritical water synthesis, rendering the particles amenable to functionalisation; printed devices require excellent dispersion of the electro-active filler within the ink. Successful functionalisation with a silane coupling agent, as observed *via* TGA, vastly improved the stability of the synthesised nanoparticles dispersed within a UV-curable poly(ethylene glycol) diacrylate (PEGDA) ink.

Further work will investigate in-flow functionalisation to improve the commercial viability of the ink production process, and the electronic performance of the hydrothermally synthesised nanoparticles will be quantified through the fabrication of printed and appropriately cured devices.

4. Conclusions

The properties of barium titanate and barium hexaferrite nanoparticles produced in supercritical water may be influenced through variation of the synthesis parameters, with a view to producing functional piezoelectric and magnetic inks, at scale, for 3D-printed device fabrication.

References

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