Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Designed 3D Architectures of High-temperature Superconductors

David C. Green[a], Martin R. Lees[b] and Simon R. Hall[a]*

a. Complex Functional Materials Group, School of Chemistry, University of Bristol, BS8 1TS, United Kingdom. Email: Simon.Hall@bristol.ac.uk.
b. Superconductivity and Magnetism Group, Physics Department, University of Warwick, Coventry, CV4 7AL, United Kingdom

Experimental Details:

Materials:

Spaghetti (own-brand durum wheat dried pasta) was purchased from The Co-operative Food (Co-operative Group Limited, UK), penne and fusilli (own-brand durum wheat dried pasta) were purchased from Sainsbury's (J. Sainsbury's plc, UK) and Honig™ Samen "Piraten Pasta" was a gift from Jamie Shenston (University of Bristol, UK) and Caroline Walker (Heinz). All metal nitrates were purchased from Sigma-Aldrich, UK. DI water was obtained from in-house MilliQ PureLab Ultra (18.2 $M\Omega cm^{-1}$). Unless stated otherwise, all materials were used as received, and with no further purification.

Y123 Aqueous Precursors Generation:

Into 200 ml DI water, 3.8301 g $Y(NO_3)_3.6H_2O$ (0.05 M) and 6.9777 g $Cu(NO_3)_2.2.5H_2O$ (0.15 M) are dissolved under stirring. Depending on the precursor required, different quantities of $Ba(NO_3)_2$ are added: 5.2268 g (0.1 M) for precursor 2:4:6 (Y:2Ba:3Cu, stoichiometric precursor), 6.5335 g (0.12 M) for precursor 2:5:6 (Y:2.5Ba:3Cu, Ba excess) or 7.8402 g (0.15 M) for precursor 2:6:6 (Y:3Ba:3Cu, Ba excess). Precursors are then stirred until full dissolution has occurred, yielding a light blue solution. When adding $AgNO_3$, 10_{wt}% of total salt in solution are added immediately before pasta rehydration (i.e. per 30 ml stock 2:6:6, total salt added (including water of crystallisation) = 2.7972 g, therefore 0.279 g $AgNO_3$ added).

Prewashing Pasta:

Before rehydration in Y123 precursor, dried durum wheat pasta is prewashed in DI water to remove the majority of poorly bound starches, soluble impurities such as metal ions (Ca^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+} and Mg^{2+}), anions (Cl^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-}) and sulfur containing materials such as vitamins and proteins as commonly found in wheat flour. Pasta is added to DI water at 90 °C at a ratio of 4 g pasta/30 ml water. Suspended pasta is stirred slowly for 1 min to ensure full submersion in the water, after which rehydration occurs at constant temperature for 20 min. Pasta is then rinsed with 30 ml cold DI water until washing water is free from suspended starch (typically 3x washings). Washed, hydrated pasta is then dehydrated over 8 hr at 45 °C.

NB: In syntheses involving 'unwashed' pasta, the pasta shapes are used as purchased directly in the following step.

Rehydration of pasta in Y123 aqueous precursor:

Typically, 30 ml Y123 precursor is heated to 90 °C (NB: $AgNO_3$, when used, is added at this point) and into which 4 g of pasta (washed or unwashed) is added and stirred gently for 1 min. Rehydration occurs at constant temperature for 20 min until the pasta is fully expanded. Successful uptake of solvated metals is indicated by emergence of a green colour given by Cu^{2+}. The dark brown colour in the presence of Ag^{+} is due to starch-mediated reduction to form Ag^{0} nanoparticles. Pasta is removed from the Y123 precursor and dehydrated over 8 hr at 45 °C, during which time the green colour intensifies due to increasing effective concentration of Cu^{2+} (and therefore Ba^{2+} and Y^{3+}) in the pasta template. No precipitation of metal salts occurs on the surface of the pasta shapes suggesting metal ions are kept homogeneous throughout the pasta shape.

Generation of Y123-rich replicas of pasta shapes and superconducting wires:

Pasta templates (both Y123 and Ag/Y123) are calcined in air at 920 °C for 2 hr with a heating ramp of 5 °C/min upon alumina slabs, yielding black replica products. Ag/Y123 replicas of spaghetti for use as superconducting wires are sintered (900 °C, 12 hr, 5 °C/min) and annealed (500 °C, 8 hr, 5 °C/min) in air on alumina slabs.

Characterisation:

Samples for transmission electron microscopy (TEM) were prepared by ethanol-dispersed, pulverised sample pipetted onto carbon-coated Cu TEM grids. TEM analysis was carried out on JEOL JEM 1200EX microscope equipped with Oxford energy dispersive X-Ray (EDX) detector. Scanning electron microscopy (SEM) samples were analysed on JEOL JSM 5600LV with similar EDX detector. Powder X-ray diffraction (pXRD) was carried out on Bruker D8 Advance diffractometer (CuKα1 radiation at λ=1.54056 nm) equipped with Lynx-eye position sensitive detector. The following JCPDS cards were used for indexing crystalline phases from pXRD analysis: Y123: 00-038-1433, Y211: 00-038-1434, Y_2O_3: 00-041-1105, CuO: 00-045-0937, $BaCO_3$: 00-045-1471, $BaSO_4$: 00-024-1035, $Ba(NO_3)_2$: 00-024-0053, Ag: 00-004-0783 and $Y_2Cu_2O_5$: 00-033-0511. Magnetic properties were measured in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) equipped with a 5T superconducting magnet. Resistance measurements were carried out using a 4-point dip probe in liquid He, with Au wires attached to the sample by Ag paint. The temperature was monitored with a LakeShore 420 Temperature Controller. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was conducted on a Netzsch STA 409 EP simultaneous thermogravimetric analyser with a TASC 414/5 controller system.

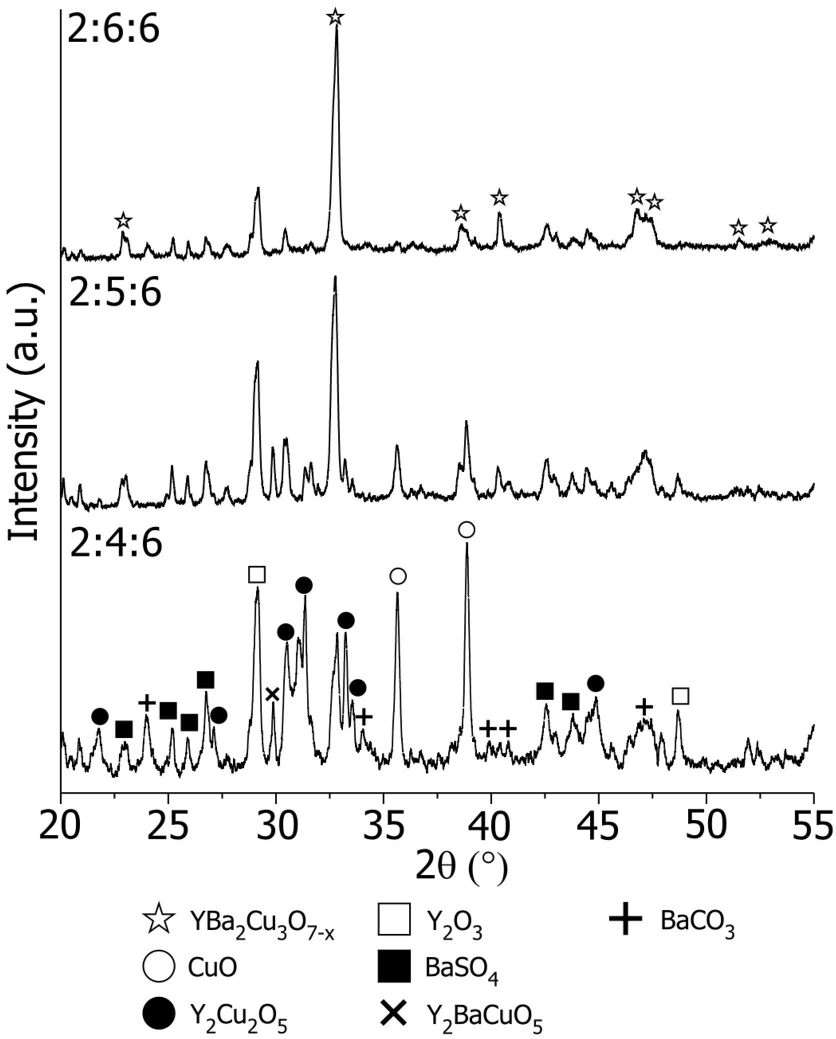

Fig. S1a: pXRD patterns of calcination of Y123 replicas of spaghetti generated from different precursors (2:4:6, 2:5:6 and 2:6:6 from bottom to top respectively). Impurity phases are indexed and labelled as shown.

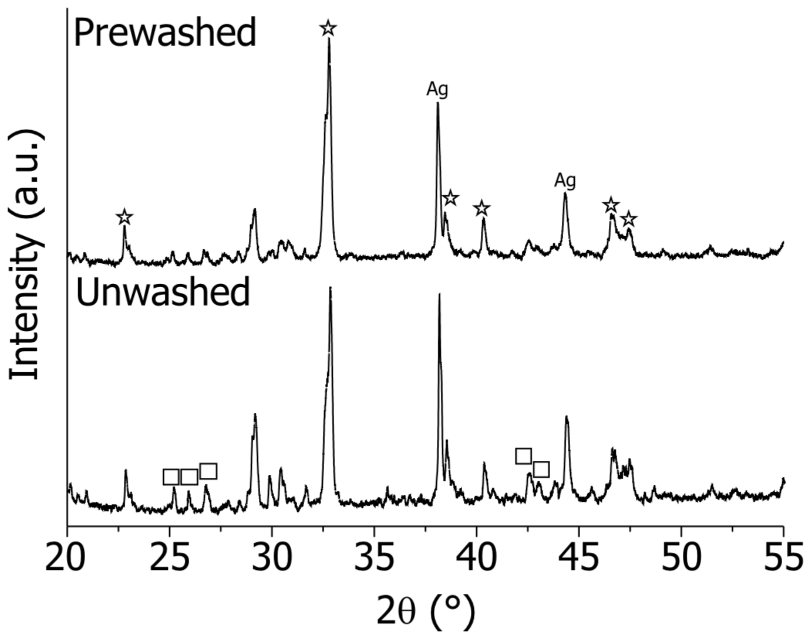

Fig. S1b: pXRD patterns comparing the Ag/Y123 replicas of spaghetti from prewashed (top) and unwashed (bottom) pasta. Y123 (star), Ag and $BaSO_4$ (square) are indexed and labelled.

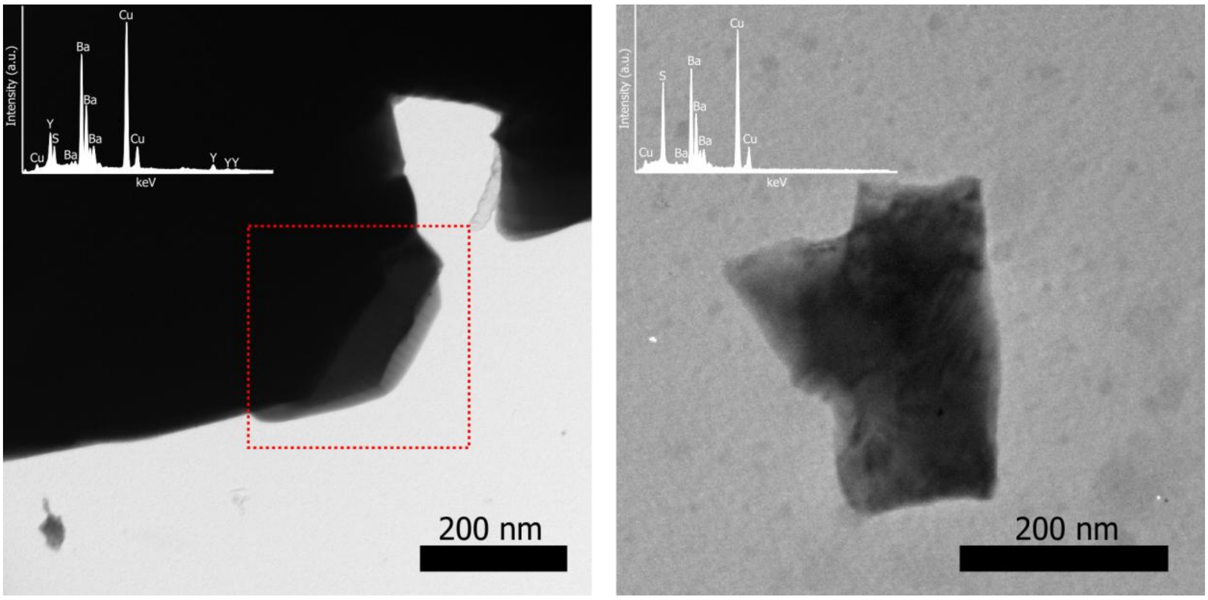

Fig. S1c: TEM images of the Ag/Y123 materials. The images show the presence of the Y123 phase (left) and $BaSO_4$ (right) as indicated by EDXA (inset).

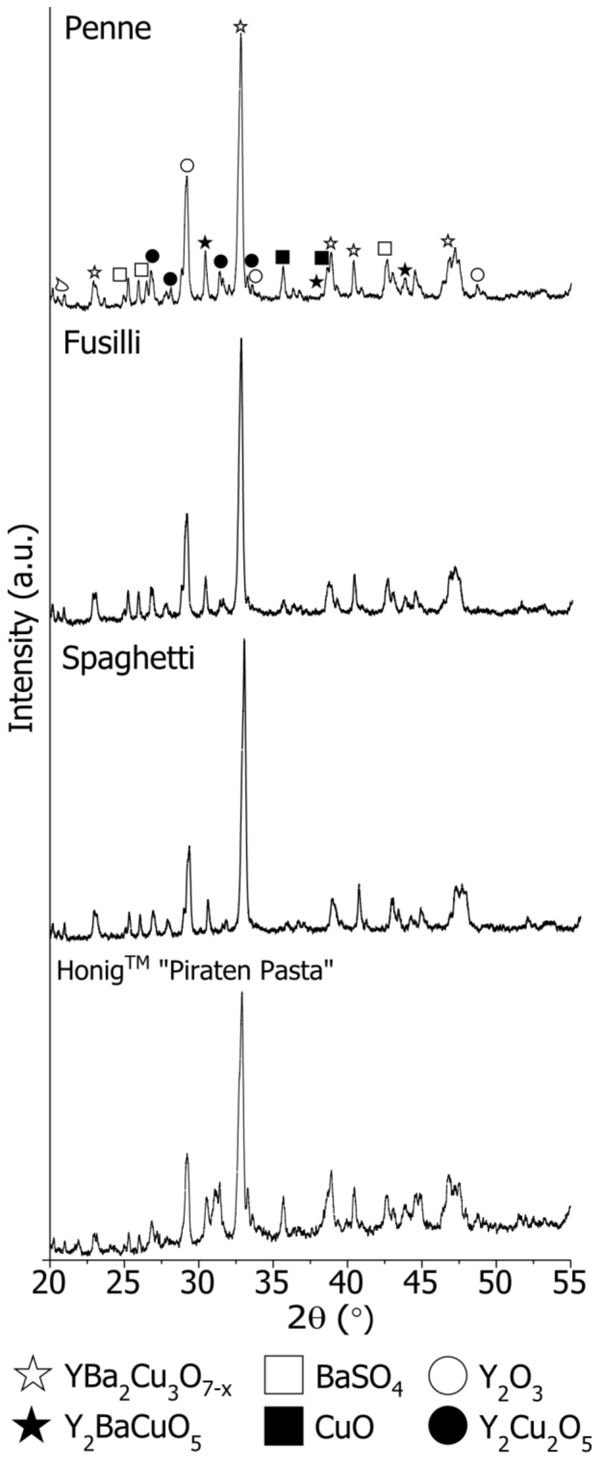

Fig. S2: pXRD analysis of Y123 replicas of various pasta shapes as labelled. Impurity phases are indexed and labelled.

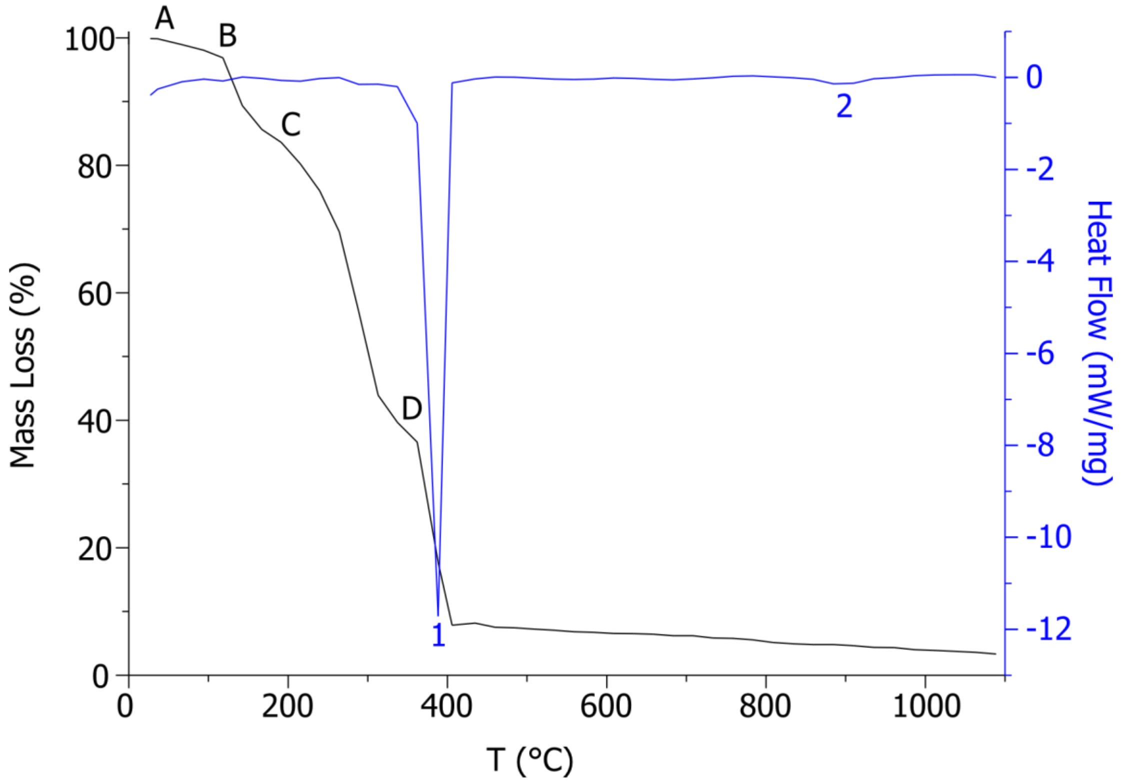

Fig. S3a: TGA (black) and DSC (blue) of the spaghetti-based precursor for Ag/Y123. The loss of volatiles/H_2O from bulk (A) and complexes (B); degradation of starch (C), and degradation of cellulose and loss of NO_x (D) are indicated, as well as changes in the heat-flow signifying endothermic processes such as full degradation of C-C bonds (1) and the melting of the carbonate/oxide components into Y123-forming eutectic (2).

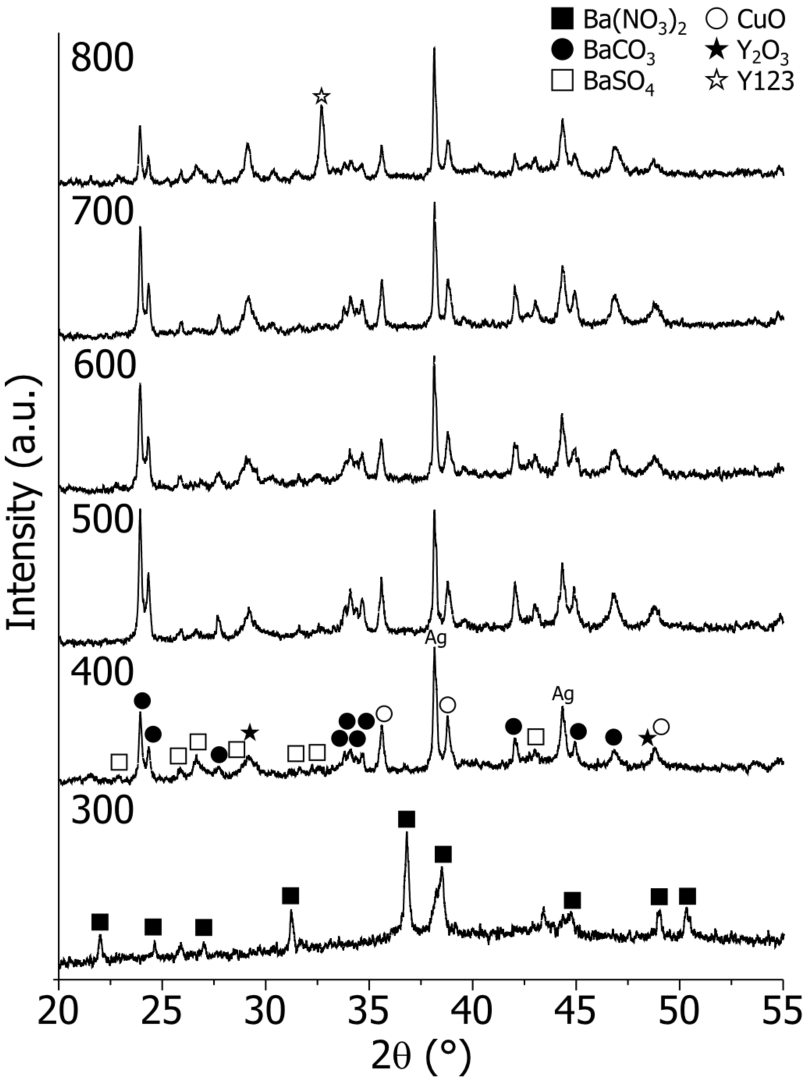

Fig. S3b: Thermal quenching study analysed by pXRD with all phases detected indexed and labelled as per the legend. Ag^0 is labelled with ‘Ag’. Progressively higher dwell temperatures are used with the lowest at 300 °C (bottom) through to the highest at 800 °C (top).

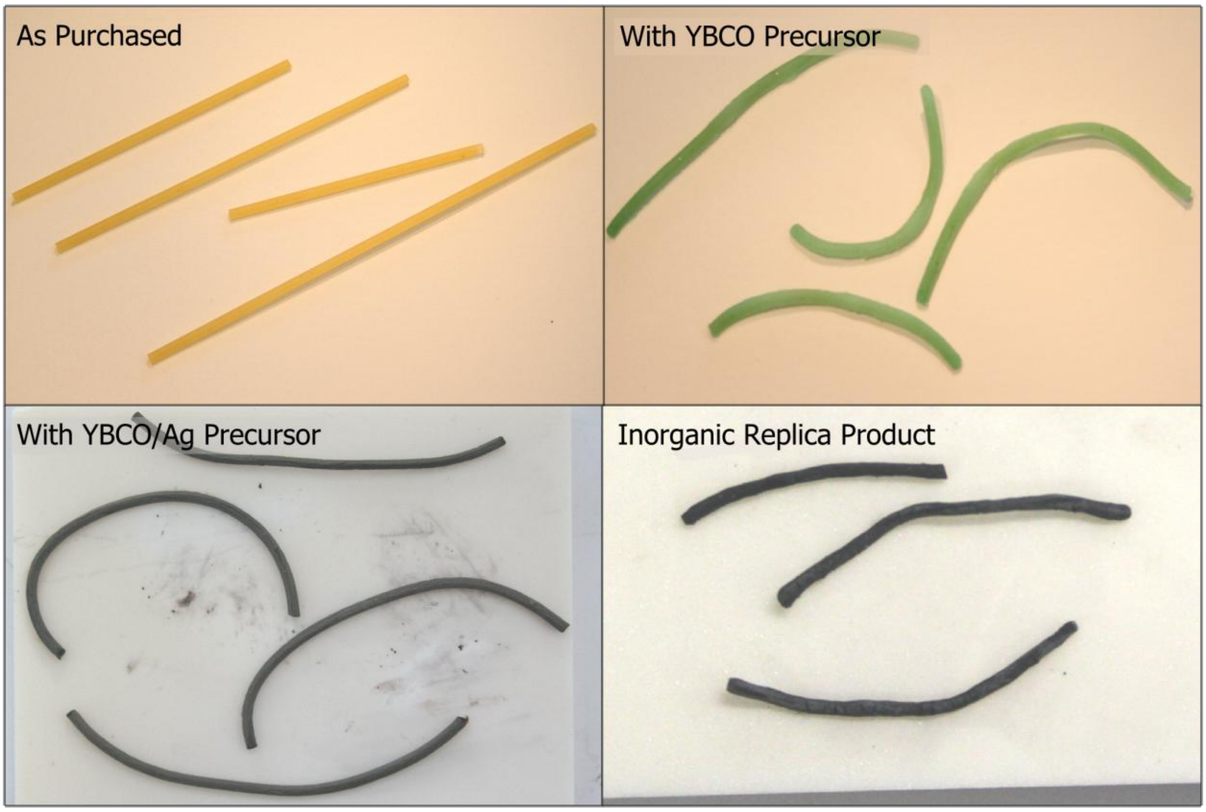

Fig. S3c. Photographs of spaghetti, Y123 or Ag/Y123 precursor spaghetti and Y123-rich replicas of spaghetti, indicating different colours exhibited from the influence of different chemical species: Cu^{2+} (green), AgNP (dark brown) and black (Y123).

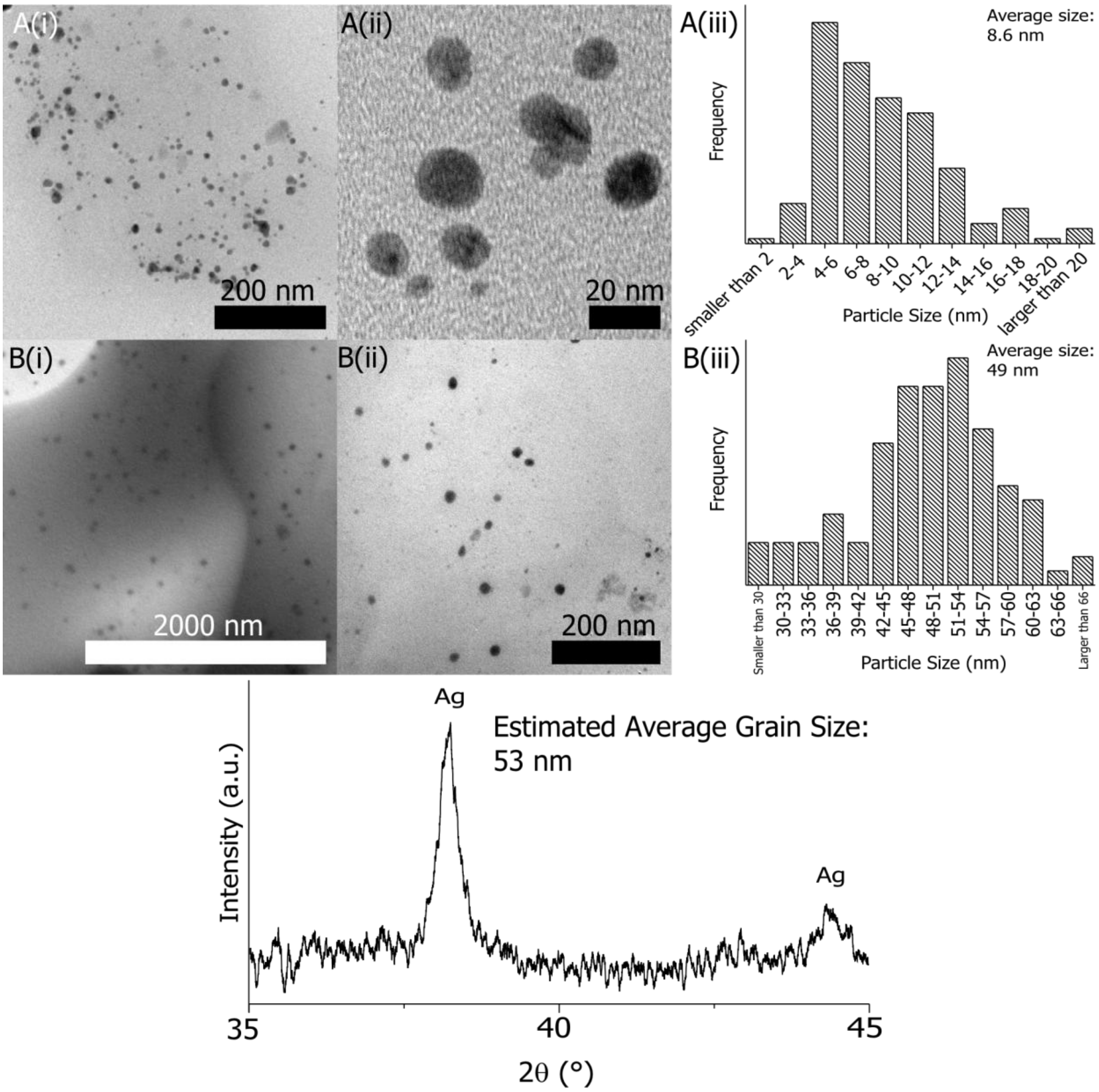

Figure S3d: TEM micrographs, particle size histogram and corresponding pXRD pattern of mascerated, uncalcined pasta precursors of Ag/Y123. A difference in nanoparticulate sizes lead to 2 different distributions of smaller (A) and larger (B) sizes with average particle sizes 8.6 nm and 49 nm respectively. Micrographs of larger nanoparticles (B) show a greater association with amorphous starch from pasta. Scherrer interrogation of pXRD yields comparable grain size estimates to the larger particles detected.

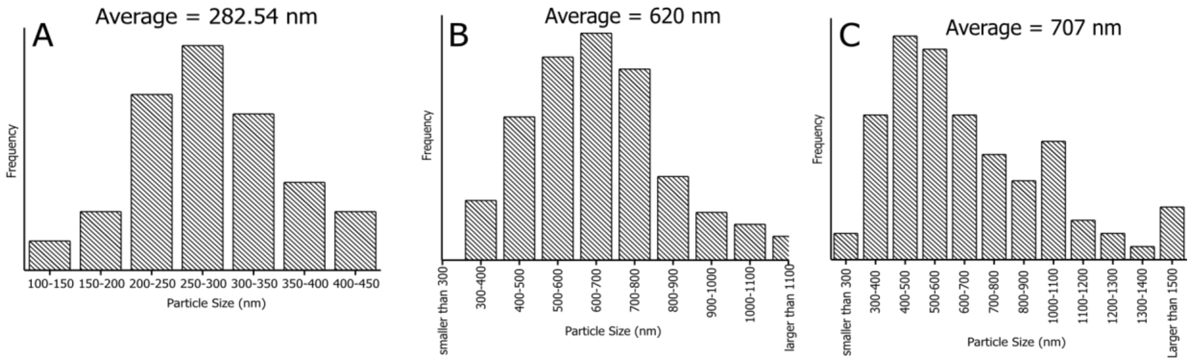

Fig. S4: Size distribution charts of particle sizes from Y123 calcined product (A), Ag/Y123 calcined product (B) and Ag/Y123 post sintering and annealing (C). Sizes are taken from SEM images and from the shortest visible length per crystallite.

Sample	**Density (mg/mm^3)**
Y123 replica of spaghetti, calcined product	0.50 ± 0.13
Ag/Y123 replica of spaghetti, calcined product	0.75 ± 0.07
Ag/Y123 replica of spaghetti, post sintering and annealing	0.98 ± 0.11

Table S1: Densities measured directly from the Y123-rich replicas.

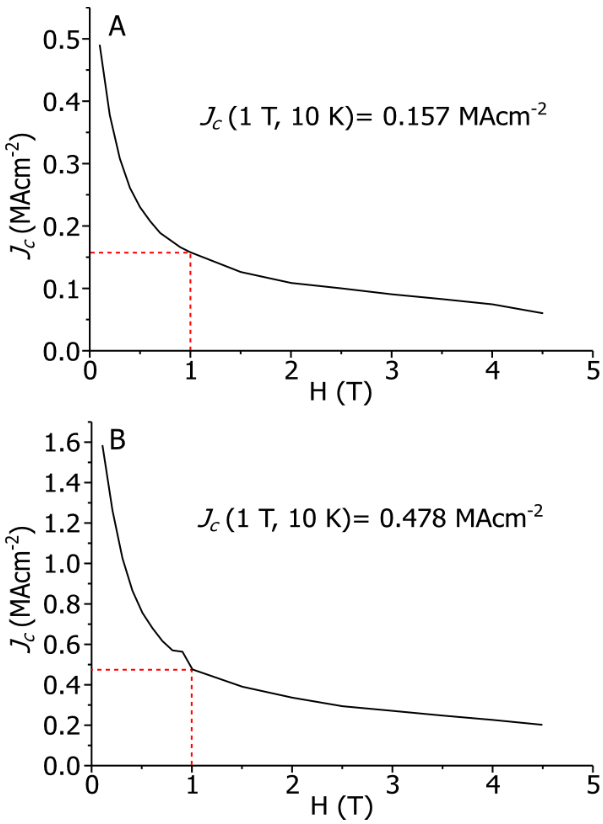

Fig. S5: Critical current density vs. H plots of the Ag/Y123 (A) and Y123 (B) replicas of spaghetti obtained at 1 T and 10 K.

Material	Mass in 100g dry spaghetti / g	Deleterious effect on Y123
Starch	62.4	
Cellulose	3.2	
Mono- and Oligosaccharides	2.7	
Protein	13	
Fe^{3+}	0.0033	Substitutes for Cu in CuO_2 planes, affecting microscopic crystal structure, leading to suppression in T_c, with T_c = 43 K with 20% doping.[2]
Ca^{2+}	0.021	Substitutes for Y^{3+} as an overdoped charge carrier, affecting oxygen content and hole concentration in CuO_2 planes, leading to suppression in T_c, with T_c = 80 K with 20% doping.[3]
Zn^{2+}	0.0014	Substitutes for Cu in CuO_2 planes, affecting charge transfer, leading to suppression in T_c, with T_c = <20 K in as little as 5% doping.[4]
Water	9.9	
Fat	1.5	
Other, Trace	7.5	

Table S2: Tabulated typical nutritional information of dry, unenriched durum wheat spaghetti and associated deleterious effects.[1]

References and Notes:

1. Data taken from United States Department of Agriculture (Nutrient Data 20420, Spaghetti, dry, unenriched).
2. S. E. Lofland, S. B. Ogale, M. Rajeswari, D. D. Chougule, S. M. Bhagat and T. Venkatesan, *IEEE Transaction on Applied Superconductivity*, 1995, **5**, 1741
3. C. T. Lin, B. Liang and H. C. Chen, *Journal of Crystal Growth*, 2002, **239**, 778
4. A. Li, Y. N. Wang, X. N. Ying, Q. M. Zhang and W. M. Chen, *Superconductor Science and Technology*, 1999, **12**, 645