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Biotemplated synthesis of an ordered macroporous superconductor with high critical current density using a cuttlebone template†

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Periodic superconducting, porous self-supporting monoliths were synthesized using cuttlebone as a morphological template; this produced a lightweight, structurally stable superconductor with a greatly improved critical current density.

High temperature cuprate superconductors are now coming into their own technologically, with the appearance of these useful materials in commercial HTS power cables, fault current limiters, transformers and generators.[1,2] The range of potential applications can be extended by controlling the crystal growth of these materials, as demonstrated previously by the synthesis of technologically important nanowires[3] and porous sponges[4] of superconducting yttrium barium copper oxide (YBCO). In the case of the latter, it was found that a porous body enabled the superconducting material to be totally perfused by cryogen, thereby leading to a faster attainment of the superconducting state and the minimization of current induced hot-spots by localized resistive heating. A sponge structure is conceptually limited however, in that it consists of a random distribution of pores of varying size and shape; by actively controlling the formation of pores, new applications for YBCO could be realized. Periodicity in porous bodies often leads to enhanced physical properties such as the creation of photonic band gaps in opaline materials and in catalysis and separation technologies.[5,6] Despite the technological importance, no report has been made on the synthesis of monolithic YBCO with a regular pore structure. Here we show that a porous structured YBCO superconductor can be made with periodic pores of well defined size and shape by the use of cuttlebone as a structure-directing crystal growth template. The cuttlebone is an ideal candidate as a template for inorganic replication and has been used previously to great effect as a route to ordered macroporous silica.[7] With a morphology designed for gas and liquids to flow through its interconnected pores with ease, both synthesis and subsequent cryogen infiltration of cuttlebone templated materials are facile procedures. We find that this synthetic approach results in a greatly increased critical current density (J_c) for YBCO, thereby making it of particular technological interest. The superconductor chosen for this study was an YBCO superconductor of the composition $YBa_2Cu_3O_{7-\delta}$ (Y123). The synthesis of the Y123 precursor was based on a previously published sol-gel method.[8] Ethylene glycol was used in the synthesis to ensure homogeneous distribution of ions and to inhibit precipitation from solution. Briefly, barium nitrate (1.307 g), yttrium nitrate (0.958 g) and copper nitrate (1.744 g) were completely dissolved in distilled water–ethylene glycol (50 : 50, 50 ml) to form a clear, blue solution. Cuttlebone (0.85 g) was soaked in an excess of this Y123 solution (approx. 15 ml), for 2 h under low vacuum to ensure complete solution infiltration. On completion, the cuttlebone was dried at 40 °C. The soaking and drying cycle was undertaken three times. Once completely dry, each sample was transferred to a crucible and calcined at 920 °C at a rate of 1 °C min^{-1} for 4 h. Samples for SEM (JEOL JSM 6330F, 30 kV) were prepared by mounting on aluminium stubs and sputter coated with platinum (Agar high-resolution Pt/Pd sputter coater) prior to observation. Samples for TEM (JEOL 1200EM, 120 kV) were dispersed in ethanol onto a nickel grid. Compressive strength testing was undertaken using an Imada HV-500N tensile/compressive strength testing rig, fitted with a DPS-50R digital force gauge. Powder XRD was carried out using a Bruker D8 Advance powder diffractometer (CuKα radiation, 1.54056 Å; 2θ values 15° to 60°, step interval 0.02°). SQUID magnetometry was performed using a Quantum Design Magnetic Property Measurement System equipped with a 5 T superconducting magnet. The measured data was not corrected for demagnetisation effects. Field cooled (FC) and zero field cooled (ZFC) DC susceptibility was measured as a function of temperature under an applied field of 1 mT. The intragrain critical current density, J_c, of the samples was determined by applying a critical state model to full magnetisation loops measured at fixed temperatures and taking the grain (particle) size from the SEM observations. Since such models are known to be inaccurate at low fields (also evident in our data, where the apparent J_c deviates from an exponential field dependence below a certain applied field value), J_c values in the text are stated at applied fields of 1 T.

SEM imaging of a section of cuttlebone (supplementary information Fig. S1†) reveals layers of parallel sheets of calcium carbonate in the form of aragonite (supplementary information Fig. S2†) supported by S-shaped pillars of the order of 500 μm in length. On completion of three soaking/drying cycles, optical microscopy revealed that the complex structure of the cuttlebone was retained, now coated with the blue superconductor precursor gel (Fig. 1a,b). Furthermore, on calcination no structural collapse was observed and the now black, oxidized replica was self-supporting. Fig. 1c shows

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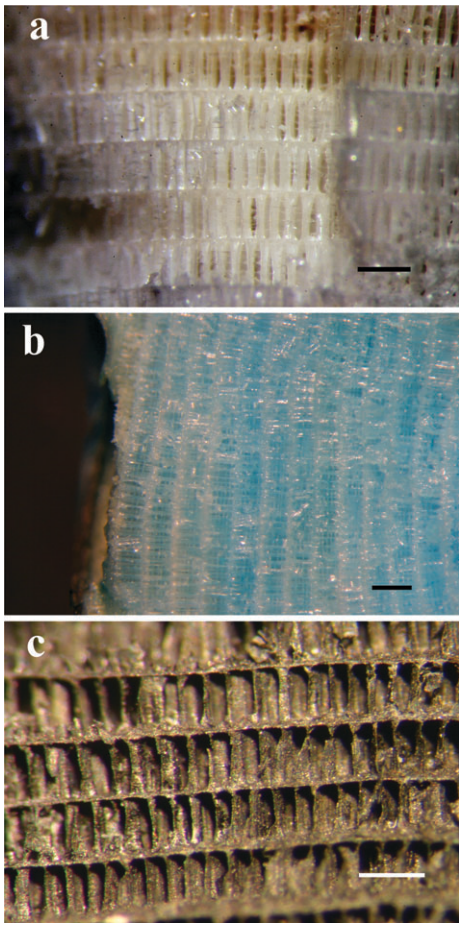

Fig. 1 Optical microscopy of (a) cuttlebone, (b) Y123 precursor gel-filled cuttlebone and (c) superconducting Y123 cuttlebone replica. Scale bars in (a) and (c), 500 μm, in (b) 1 mm.

the clearly defined S-shaped pillars and lamellae in the calcined material. The spacings between the lamellae are approx. 450 μm which correlate well with pure cuttlebone. This implies that shrinkage did not occur and was most likely due to the presence of oxides of calcium from the cuttlebone, retaining the overall macrostructural morphology during and after calcination. TEM and SEM analyses show the presence of sub-micron sized crystallites which electron diffraction confirms as Y123. Additionally, elemental mapping indicates the presence of calcium salts of the order of 5 microns in size (supplementary information Fig. S3†).

SQUID magnetometry showed that the superconducting critical temperature (T_c) of the replica was 93 K (Fig. 2), a value which confirms optimum oxygenation of the Y123.[9,10] The open architecture of the cuttlebone is therefore providing an exceedingly efficient oxygenation of the superconductor during calcination. This obviates the need to calcine under flowing oxygen in order to produce a high-quality Y123 material, thereby lowering the cost and reducing complexity of synthesis.

The effect on J_c of synthesizing the superconductor in this morphology is considerable. The critical current density of the cuttlebone templated Y123 was measured at 1.6 $MAcm^{-2}$ at 10 K and 1 T field. This is almost two orders of magnitude

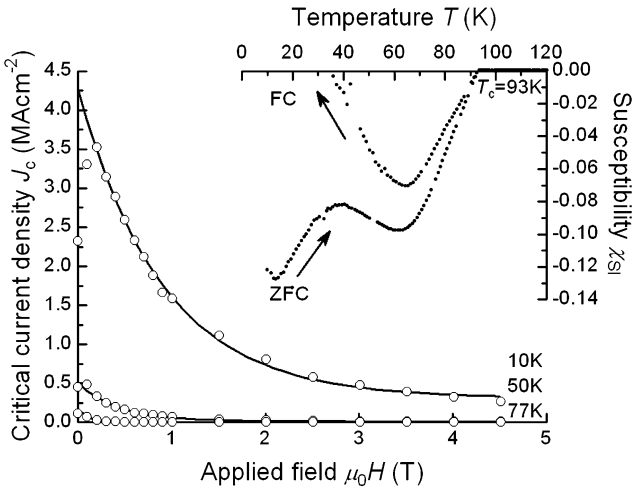

Fig. 2 SQUID magnetometry of superconducting cuttlebone replica.

higher than that observed in a commercially available Y123 powder (Aldrich 99.9% — average particle size 5 μm), for which SQUID magnetometry revealed a T_c of 92 K and a critical current density of 0.02 $MAcm^{-2}$ at 10 K and 1 T field. From the behaviour of the field-cooled plot, it is apparent that remnant impurities in the calcined mixture contribute to the strong paramagnetic upturn at low temperatures. XRD confirms this, identifying three phases present in the final material (Fig. 3), with Y123 present as a minority phase. It is clear that the lime and slaked lime majority phases are present due to thermal breakdown of the aragonitic cuttlebone. Attempts to remove the moderately soluble calcium phases by solvation resulted in total collapse of the macroporous monoliths. Whilst embuing these materials with macroporous morphology, these phases do not otherwise encumber the superconductivity of the cuttlebone replicas.

In terms of mechanical strength, the cuttlebone-templated superconductors are self-supporting but very weak. Compressive strength testing failed to determine a value, as these materials were weaker than the force gauge could measure (<1.5 kPa). Mechanical strength was improved by the addition of silver to the synthesis. The incorporation of silver into YBCO materials has been shown previously to improve the structural integrity of the superconductor by increasing the

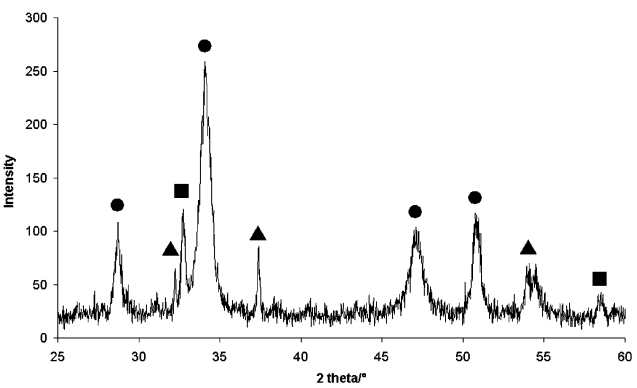

Fig. 3 PXRD of cuttlebone-templated Y123. Peaks marked (●) are $Ca(OH)_2$, (▲) CaO and peaks marked (■) are from Y123.

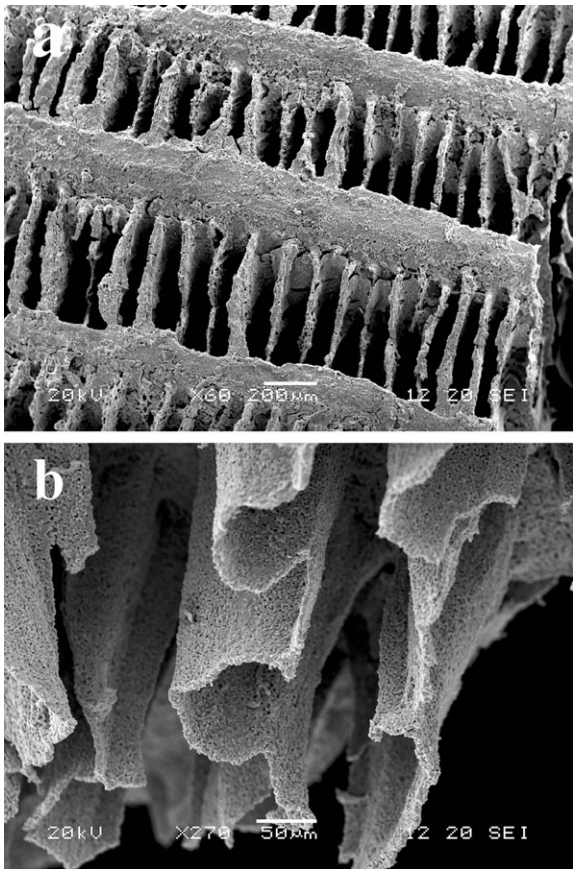

Fig. 4 SEM images showing Ag-doped Y123 cuttlebone replicas. Scale bar in (1) is 200 μm, in (b) 50 μm.

density, providing ductility and enhancing YBCO grain intergrowth and promoting larger crystal sizes through silver acting as a low melting flux.[11–13] In this work we introduced silver into the synthesis mixture by the simple addition of approx. 10 wt% of silver nitrate (as compared to total nitrates present).

After calcination, the monoliths were noticeably more structurally stable. Compressive strength testing confirmed this, with monoliths capable of withstanding a compressive strength of 27.95 kPa, a figure comparable with certain roofing materials used in the construction industry. EDXA revealed the presence of silver in the material (supplementary information Fig. S4†), and PXRD showed more pronounced peaks due to Y123 than in the undoped sample (supplementary information Fig. S5†), confirmation that the silver is promoting a more pronounced crystalline structure.[4,13] SEM images show that the silver doped replicas retain the cuttlebone morphology exceedingly well, even to the extent that the fine structure of the S-shaped pillars are reproduced in detail (Fig. 4). TEM revealed that the crystallite size was now 3 μm ± 0.2 μm, larger than seen in the undoped samples (supplementary information Fig. S6†). This increase in crystallite size has ramifications for the electronic behaviour of these materials, as an increase in crystallite size can often lead to a decrease in critical temperature and current. SQUID magnetometry confirms this, with a pronounced decrease in both T_c (to 73 K) and J_c (to 0.16 MA cm^{-2}) of the silver doped samples (supplementary information Fig. S7†). It is apparent therefore, that a balance must be struck between an improvement in compressive strength and the electronic performance of the superconducting monolith.

Finally, we note that the weight of 1 cm^3 of superconducting cuttlebone replica is 0.06 g, compared to 6.38 g in the case of an equivalent sized monolith of pure Y123. With an overall decrease in mass of two orders in magnitude, these materials could well find application in areas where weight is of critical importance, such as space-based and mobile device technologies. It is envisaged too, that our method could apply equally well in the synthesis of light and porous giant magnetoresistive, piezoelectric and ferromagnetic materials.

In conclusion, we have demonstrated that cuttlebone is an excellent template for the controlled crystallization of the superconductor Y123 in an ordered, macroporous morphology with a greatly improved critical current density. Improving J_c is one of the key driving forces in superconductor materials research and to be able to generate such a large increase in critical current density by a considered architectonic approach, will hopefully stimulate further research in templated crystallization of these fascinating and technologically important materials.

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