Chem. Mater. **2007,** *19,* 647−649

Use of the Polysaccharide Dextran as a Morphological Directing Agent in the Synthesis of High-T_c Superconducting $YBa_2Cu_3O_{7-\delta}$ Sponges with Improved Critical Current Densities

Dominic Walsh,[†] Stuart C. Wimbush,[‡] and
Simon R. Hall*[,†]

Centre for Organized Matter Chemistry,
School of Chemistry, University of Bristol, Cantock's Close,
Bristol BS8 1TS, United Kingdom, and National Institute for
Materials Science, International Center for Young Scientists,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received November 9, 2006
Revised Manuscript Received January 8, 2007

The key property of practical high-temperature superconductors is the amount of current able to be carried while in the superconducting state. This critical current density (J_c) is adversely affected by crystallite grain boundaries,[1−3] and as a result, control of crystallization is an extremely active area of research.[4,5] However, this invariably involves either epitaxial growth of thin films or melt-texturing of bulks and may involve complex and sensitive syntheses, unlike the simple and benign approaches to crystallographic control that are characteristic of biomimetic materials chemistry.[6−8] Here we demonstrate that synthesis of $YBa_2Cu_3O_{7-\delta}$ (Y123) using the polysaccharide dextran derived from the bacteria *Leuconostoc spp*. achieves not only an extremely effective oxygenation of the superconductor (thereby obviating the need for calcination under flowing oxygen) but also an in situ biomimetic template directing of the crystal morphology resulting in high J_c, homogeneous superconducting sponges with nanoscale crystallinity. In addition, the sol−gel synthesis allows for dopants such as silver and sodium to be easily introduced in order to improve the stuctural stability of the sponges. Superconducting sponges are of interest for practical applications such as fault current limiters and superconducting bearings, owing to their high thermal shock resistance and more uniform cryogenic cooling.[9,10] This work represents the first time that a high-temperature superconductor has been created using a biopolymer as a self-sacrificial template. Recently, it has been demonstrated that control over the crystal morphology in Y123 superconductors can be effected by the incorporation of a biopolymer into the sol−gel solution synthesis protocol[11] and that the biopolymer dextran can be used as a sacrificial template in the synthesis of metallic sponges.[12] In this work, Y123 sponges were prepared by the admixing of dextran with a solution of metal nitrate salts of the correct stoichiometry to form Y123. Dextran was obtained from Fluka, and yttrium nitrate, barium nitrate, copper nitrate, silver nitrate, and sodium chloride were all obtained from Aldrich (99.99%). In a typical synthesis, sponges were prepared by the addition of dextran (20 g, M_r = 70 000) to a superconductor precursor solution (10 mL). The precursor solution was prepared by the dissolution of $Y(NO_3)_3{\cdot}6H_2O$ (1.915 g, 0.05 M), $Ba(NO_3)_2$ (2.613 g, 0.1 M), and $Cu(NO_3)_2{\cdot}2.5H_2O$ (3.489 g, 0.15 M) in 100 mL of H_2O. Dextran and precursor solution were mixed together in a crucible to form a light blue, viscous paste and left for 1 day at room temperature to harden. The resulting paste was then heated to a temperature of 920 °C at a ramp rate of 10 °C/min in a Carbolite furnace and held at that temperature for 2 h, cooling subsequently to room temperature at a rate of approximately 2 °C/min. Silver-doped Y123 sponges were prepared in the same manner as above, with the addition of $AgNO_3$ (0.8 g, 4.7 mM) to the precursor solution. After mixing the silver-doped solution with dextran, the paste gradually changed color from a light blue to a dark red-black over a period of 30 min. Calcination was performed on silver-doped samples as described above. Sodium-doped Y123 sponges were prepared by sprinkling finely ground NaCl (0.04 g) across the surface of the hardened Y123−dextran composite paste prior to calcination. The calcination protocol was the same as above. Samples for scanning electron microscopy (SEM; JEOL JSM 6330F, 30 kV) were prepared by mounting on aluminum stubs and sputter coating with platinum (Agar high-resolution Pt/Pd sputter coater) prior to observation. Compressive strength testing was undertaken using an Imada HV-500N tensile/compressive strength testing rig, fitted with a DPS-50R digital force gauge. Powder X-ray diffraction (XRD) was carried out using a Bruker D8 Advance powder diffractometer (Cu Kα radiation, 1.540 56 Å; 2θ values 15−55°, step interval 0.02°). Superconducting quantum interference device (SQUID) magnetometry was performed using a Quantum Design Magnetic Property Measurement System equipped with a 5 T superconducting magnet. The measured data were not corrected for demagnetization effects. Field cooled (FC) and zero field cooled (ZFC) direct current susceptibility was

---

[*] To whom correspondence should be addressed. E-mail: simon.hall@bristol.ac.uk.

[†] University of Bristol.

[‡] International Center for Young Scientists. Current address: Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, U.K.

(1) Hilgenkamp, H.; Mannhart, J. *Rev. Mod. Phys.* **1994**, *74*, 485−549.
(2) Dimos, D.; Chaudhari, P.; Mannhart, J. *Phys. Rev. B* **1990**, *41*, 4038−4049.
(3) Mannhart, J.; Chaudhari, P.; Dimos, D.; Tsuei, C. C.; McGuire, T. R. *Phys. Rev. Lett.* **1988**, *61*, 2476−2479.
(4) Obradors, X.; Puig, T.; Pomar, A.; Sandiumenge, F.; Mestres, N.; Coll, M.; Cavallaro, A.; Roma, N.; Gazquez, J.; Gonzalez, J. C.; Castano, O.; Gutierrez, J.; Palau, A.; Zalamova, K.; Morlens, S.; Hassini, A.; Gibert, M.; Ricart, S.; Moreto, J. M.; Pinol, S.; Isfort, D.; Bock, J. *Supercond. Sci. Technol.* **2006**, *19*, S13−S26.
(5) Lin, Y.; Wang, H.; Maiorov, B.; Hawley, M. E.; Wetteland, C. J.; Arendt, P. N.; Foltyn, S. R.; Civale, L.; Jia, Q. X. *J. Mater. Res.* **2005**, *20*, 2055−2060.
(6) Mann, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3392−3406.
(7) Mann, S. *J. Chem. Soc., Dalton Trans.* **1997**, *21*, 3953−3962.
(8) Davis, S. A.; Dujardin, E.; Mann, S. *Curr. Opin. Solid State Mater. Sci.* **2003**, *7*, 273−281.
(9) Noudem, J. G.; Reddy, E. S.; Schmitz, G. J. *Physica C* **2003**, *390*, 286−290.
(10) Noudem, J. G.; Guilmeau, E.; Chateigner, D.; Lambert, S.; Reddy, E. S.; Ouladdiaf, B.; Schmitz, G. J. *Physica C* **2004**, *408−410*, 655−656.
(11) Hall, S. R. *Adv. Mater.* **2006**, *18*, 487−490.
(12) Walsh, D.; Arcelli, L.; Ikoma, T.; Tanaka, J.; Mann, S. *Nat. Mater.* **2003**, *2*, 386−390.

10.1021/cm0626684 CCC: $37.00

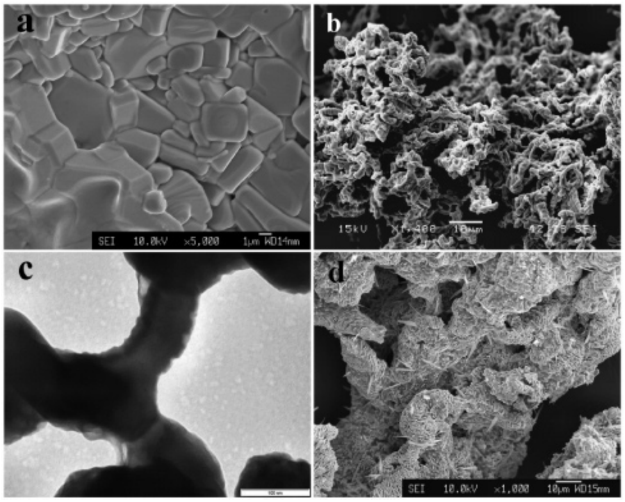

Figure 1. SEM images of (a) the control Y123 sample and (b) a dextran-templated Y123 sponge and (c) TEM image showing detail of the gel-like nature of the dextran-templated Y123 sponge and (d) a silver-doped dextran-templated Y123 sponge. Scale bar in part a is 1 μm, in parts b and d is 10 μm, and in part c is 100 nm.

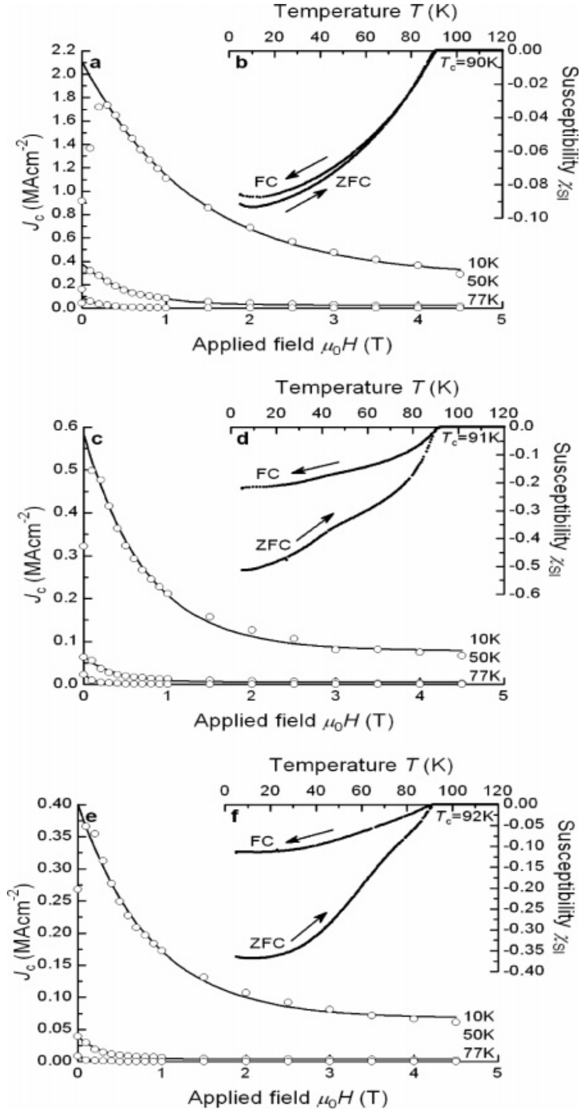

Figure 2. SQUID magnetometry showing critical current densities (J_c) and critical temperatures (T_c) of various superconducting sponges: in parts a and b, a dextran-templated Y123 sponge; in parts c and d, a silver-doped dextran-templated Y123 sponge; and in parts e and f, a sodium-doped dextran-templated Y123 sponge.

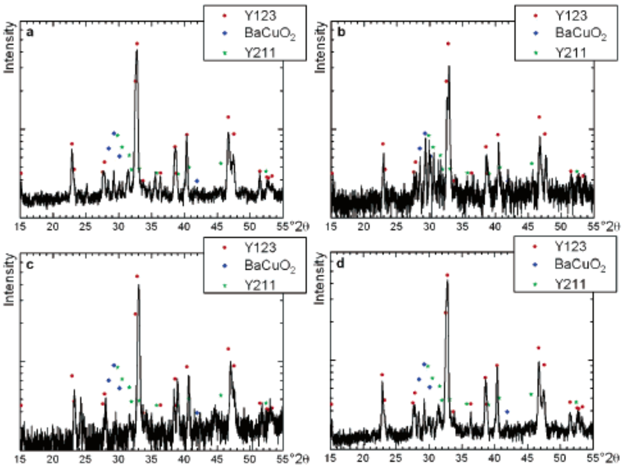

Figure 3. XRD patterns of (a) a dextran-templated Y123 sponge, (b) the control Y123 sample (without dextran), (c) a silver-doped dextran-templated Y123 sponge, and (d) a sodium-doped dextran-templated Y123 sponge.

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 magnetization loops measured at fixed temperatures, assuming a nominal sample density of 6.383 g/cm^3 and taking the grain (particle) size from the SEM observations. Because 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.

Calcination was performed in air primarily to achieve crystallization of the superconducting phase but also to foam the dextran, thereby sparging the rapidly oxidizing synthesis mixture and controlling crystal growth and overall macromorphology. In contrast to Y123 synthesized without dextran present (Figure 1a), which shows the typical polydispersity in terms of crystal size and morphology, a Y123 dextran-templated sponge (Figure 1b) has a uniform, macroporous, open architecture. Attempts to measure the compressive strength of these materials were unsuccessful, as the resistivity to compression of the highly porous sponge was off the low end of the scale (<1.5 kPa). Transmission electron microscopy (TEM) imaging confirms that the fine structure of the Y123 sponge consists of a gel-like composition with a typical strut size of around 60 nm (Figure 1c).

SQUID magnetometry shows that this material is superconducting, with an onset critical temperature (T_c) of 90 K (Figure 2b). In this sample, the FC data and the ZFC data are extremely similar; that is, the magnetization is highly reversible, implying weak bulk pinning. Nonetheless, a high critical current density of 1.8 kA cm^{-2} at 77 K and 1 T field is obtained, rising to 1.1 MA cm^{-2} at 10 K, 1 T (Figure 2a), which must be attributed to surface pinning of the porous structure, as well as its small crystallite size. XRD (Figure 3a) shows strong peaks corresponding to Y123, with only minor indications of other constituents. This contrasts sharply with the control (dextran-free) Y123 sample as under the same calcination conditions; that material is dark green in color, suggesting the presence of an additional phase. This is confirmed by XRD (Figure 3b) which, in addition to the peaks due to Y123, shows prominent peaks from the Y211 (Y_2BaCuO_5, "green") phase, as well as an associated $BaCuO_2$ phase. Secondary phases can be detrimental to the performance of superconducting materials, although in the case of Y211 inclusions within a Y123 bulk, the critical current is actually improved as a result of enhanced flux pinning by submicrometer Y211 grains.[13,14] In terms of microstructure, however, secondary phases are almost always detrimental to the morphological integrity of the sample. SEM images of the control sample indeed show a wide size distribution of crystals with many inclusions (Figure 1a). A commercially obtained Y123 powder (Aldrich 99.9%—average particle size 5 μm) was therefore also investigated as a monophasic control. It was found to have a T_c of 92 K and a critical current density of just 0.04 kA cm^{-2} at 77 K, 1 T, and 0.02 MA cm^{-2} at 10 K, 1 T (see Supporting Information). These values are over an order of magnitude lower than those observed in the Y123 sample synthesized in the presence of dextran. The inclusion of silver in the Y123 sponges was also investigated. Silver is ubiquitous in YBCO research as a means to improve mechanical strength and grain connectivity, usually leading to an increase in J_c.[15,16] Silver inclusions are typically introduced through a diffusion-doping approach, which results in islands of silver around 10 μm in diameter. In this work, we introduced silver into the synthesis mixture by the simple addition of approximately 10 wt % of silver nitrate (as compared to total nitrates present). SEM (Figure 1d) showed that the addition of silver resulted in a more pronounced crystalline structure, the sponge with well-defined 500 nm sized crystallites now able to be manipulated without structural collapse. Compressive testing confirmed this, with the compressive strength of these sponges increased to 15.69 kPa. XRD (Figure 3c) confirmed that the Y123 phase was retained in this material. SQUID magnetometry revealed that the T_c for this material was 91 K (Figure 2d), with a J_c of 0.6 kA cm^{-2} at 77 K, 1 T, and 0.2 MA cm^{-2} at 10 K, 1 T (Figure 2c). The increased splitting of the FC and ZFC curves with respect to the pure dextran-templated sample implies an improved bulk pinning as a result of the incorporation of silver. The role of silver as a flux-pinning agent is confirmed as when the amount of silver is reduced by approximately 80%, the critical current is drastically reduced. At 77 K and 1 T, sponges with the lower amount of silver have a have a J_c of only 0.008 kA cm^{-2}, rising to 0.02 MA cm^{-2} at 10 K and 1 T, despite the reduced 200 nm crystallite size. The magnetization also becomes much more reversible, reminiscent of the undoped sample, although a strong irreversibility begins to develop at low temperatures. The addition of sodium chloride (NaCl) was also investigated in an effort to improve the mechanical properties of the sponges as well as to provide nanoparticulate flux pinning centers. NaCl has traditionally been added to ceramic materials to improve their structural stability ("salt glazing").[17] SEM revealed that sodium-doped Y123 sponges were crystalline and more structurally stable, resembling the fully silver-doped sponges in appearance and dimension. Compressive strength testing again confirmed an increase in compressive strength of these sponges, with values of 18.83 kPa. XRD (Figure 3d) showed that the sample was predominantly Y123. SQUID magnetometry showed that the T_c for this material was 92 K (Figure 2f), with a J_c of 0.2 kA cm^{-2} at 77 K, 1 T, and 0.2 MA cm^{-2} at 10 K, 1 T (Figure 2e). The slightly higher T_c and increased irreversibility of this sample compared to the silver-doped one suggests that sodium doping may be a viable avenue of investigation for improving the flux-pinning properties of structurally stable Y123 sponges prepared via this technique. For both silver and sodium doping, the addition of monovalent metal ions to the Y123−dextran composite induces the development of pronounced crystallites which grow in intimate contact along the foam structure formed by the dextran as it is calcined, resulting in an increased mechanical stability.

In conclusion, we have demonstrated that by performing an in-air calcination of Y123 in the presence of the polysaccharide dextran, sponge-like architectures of superconducting material are produced. In addition, we have shown that inclusion of silver or sodium metal ions to the Y123 sponges is a facile procedure. By simply controlling the crystal morphology of Y123 during synthesis, we have created a highly porous, fine grained superconductor in which the critical current density is improved over that available commercially by over an order of magnitude.

Acknowledgment. D.W. and S.R.H. gratefully acknowledge the Royal Society and the Engineering and Physical Sciences Research Council, U.K., for financial support.

Supporting Information Available: Figure S1, SQUID magnetometry of a commercially available Y123 powder (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0626684

---

(13) Giovannelli, F.; Monot-Laffez, I. *Supercond. Sci. Technol.* **2002**, *15*, 1193−1198.

(14) Murakami, M.; Fujimoto, H.; Gotoh, S.; Yamaguchi, K.; Koshizuka, N.; Tanaka, S. *Physica C* **1991**, *185−189*, 321−326.

(15) Fuchs, G.; Krabbes, G.; Müller, K. -H.; Verges, P.; Schultz, L.; Gonzalez-Arrabal, R.; Eisterer, M.; Weber, H-W. *J. Low Temp. Phys.* **2003**, *133*, 159−179.

(16) Fonseca, F. C.; Muccillo, R. *Physica C* **1996**, *267*, 87−92.

(17) Rogers, P. *Salt Glazing*; A & C Black: London, 2002.