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A Macroporous Perovskite Manganite from Colloidal Templates with a Curie Temperaure of 320 K

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Recently, there has been extensive interest in the creation of porous materials with three-dimensional (3D) periodicity due to potential applications in optical filter and switch, catalysis, and chemical sensor.[1] A variety of porous materials such as metals, semiconductors, and mono-oxides have been synthesized by replicating colloidal crystal templates.[2] In this method, the corresponding precursor solution infiltrates the interstitial voids of a crystal template and solidifies without disrupting the parent framework. A new porous material with long-ranged periodic structure is then created by subsequently removing the template. An important feature of this method is that the resulting spherical voids originally occupied by the templates are highly ordered and interconnected via small channels. The porous product can thus be considered a new type of 3D nanoporous networks in which the widths of the interconnecting channels are dependent upon the surface area of contact between colloids in the templates and wetting of the template by precursor solution.

Thus far, this templating method has been used to create porous mono-oxides primarily suitable for optical and chemical applications.[3] Porous materials for electronic and magnetic applications have received much less attention, partly because they consist of complex metal oxides and it is therefore difficult to synthesize the corresponding precursor solutions. In this communication, we report the synthesis of a porous ferromagnetic (FM) perovskite manganite, $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), which is known to be a colossal magnetoresistance material.[4] This is the first example of an artificial 3D ordered FM network replicated from a colloidal crystal template. Potential applications for such a magnetoresistive FM material are diverse, including a field tunable optical switch, a magnetic ion separator, and a magnetoresistance sensor.

The first step in this method was to fabricate a well-ordered colloidal template using nearly monodisperse polymethyl methacrylate (PMMA) spheres, which were prepared using a modified version of literature methods.[5] The key consideration in the synthesis of the porous LCMO material was to make a precursor solution that easily infiltrated the interstitial voids in the

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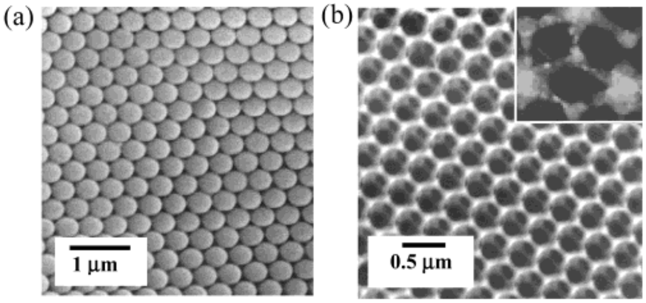

Figure 1. (a) Typical SEM micrograph of PMMA colloidal templates. (b) SEM image showing the nanowired framework of macroporous LCMO oxides. TEM image of the same sample is given in the inset, showing the three channels in the bottom of the spherical pore.

PMMA colloids of the template and that adhered strongly to the template via a condensation reaction. We employed a sol−gel method in our synthetic process to achieve complete filling of the template. A precursor solution was prepared using $La(CH_3CO_2)_3 \cdot xH_2O$ (0.14 mmol, Aldrich 99.9%), $Ca(CH_3CO_2)_2 \cdot H_2O$ (0.06 mmol, Aldrich 99+%), and $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (0.20 mmol, Aldrich 99+%) as the starting reagents.[6] A stoichiometric mixture of the metal acetates with the LCMO composition was first dissolved in 50 mL of 2-methoxyethanol (anhydrous, Aldrich 97%), to which 2 mL of HNO_3 (DC Chemical Co., 60%) was added. The solution was distilled at 125 °C until the volatile components were removed. The condensed solution was diluted with 2-methoxyethanol and the distillation step was repeated until the concentration of the Mn ion was about 1 M. The resulting metal alkoxide solution was then diluted with ethanol (Hayman, 99.9%) such that the typical volume ratio of the precursor solution to ethanol was about 0.25. The viscous solution was then gently dropped until the millimeter-thick PMMA template was completely soaked with the solution. The filling procedure was repeated several times at regular intervals. After the solution dried overnight, the PMMA colloids were removed by sintering at 800 °C under an O_2 atmosphere, leaving behind the porous LCMO material with spherical voids of diameter about 340 nm. The Brunauer−Emmett−Teller (BET) surface area determined by nitrogen sorption measurements was 24.23 m^2/g, which is in the range of typical macroporous oxides.[7]

A field emission scanning electron microscopy (SEM) image of the PMMA template, given in Figure 1a, consists of the PMMA spheres in large 3D ordered arrays of colloids with close-packed stacking. On the basis of the SEM image, the average diameter of the colloids was estimated to be about 400 ± 10 nm. Porous LCMO networks were replicated from PMMA templates and the interstitial voids of which were filled with the precursor solution. As can be seen in Figure 1b, the LCMO replicas exhibited considerable 3D ordering of the voids originally occupied by the PMMA colloids. The average diameter of the voids was approximately 340 ± 10 nm, which is 15% smaller than that of the parent PMMA colloids, indicating that the polymer/oxide composite underwent shrinkage during sintering. Similar reductions have been observed in macroporous metal films replicated from polystyrene templates.[8] Each spherical pore in the LCMO framework is connected to 12 neighboring ones through small channels. The average size of these channels that results from the contact areas between the PMMA colloids was about 150 nm. Thus, the width of the resulting surface between channels ranged from 20 to 70 nm, which is in the range of the widths of $La_{0.5}M_{0.5}MnO_3$ (M = Ba, Sr) nanowires prepared by hydrothermal reaction.[9] Therefore, the porous LCMO materials can be viewed as 3D ordered networks linked by nanowires of tens of nanometers thickness.

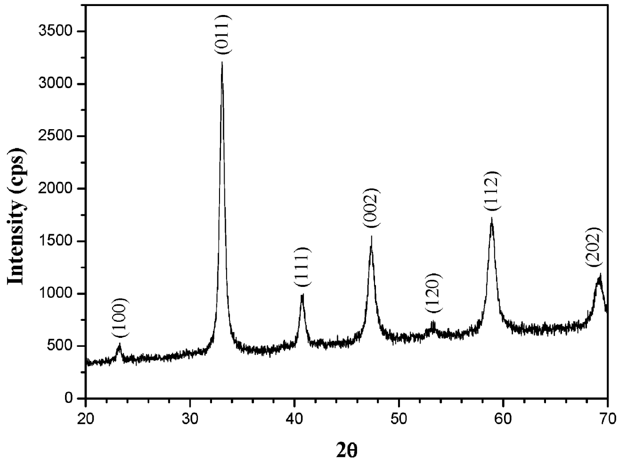

Figure 2. X-ray powder diffraction pattern of porous LCMO material after sintering at 800 °C under the O_2 atmosphere.

This “nano-networking” feature of the porous LCMO material was also evidenced by the X-ray diffraction data shown in Figure 2 in which all the diffraction peaks are noticeably broadened. This peak broadening was due to the small grain size. It was thus very difficult to index the diffraction peaks on an orthorhombic cell, although this is the actual symmetry of the bulk LCMO compound. Instead, the diffraction pattern was indexed on a pseudo cubic perovskite cell with a lattice parameter of $a = 3.841(2)$ Å.

The temperature-dependent magnetization curve of the porous LCMO material is presented in Figure 3. For comparison, magnetization data for a single crystal of LCMO grown by the floating zone method are also given.[10] It is interesting to note that the magnetic moment of the porous sample is smaller than that of the single-crystal sample. We propose that the most likely cause of the reduced moment in the porous sample is the presence of a superparamagnetic phase resulting from nanocrystalline domains in the FM matrix. This conjecture is supported by the network structure of the porous LCMO material, which can be viewed as entanglements of nanowires of tens of nanometers in width. The field (H) dependent magnetization data, given in the inset of Figure 3, also implies the existence

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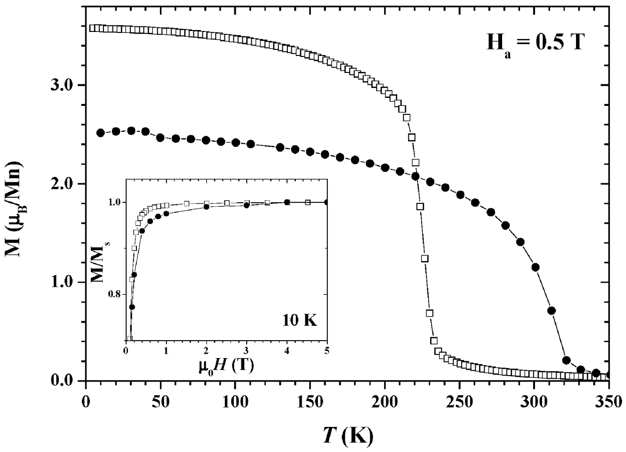

Figure 3. (a) Temperature-dependent magnetization curves of porous (filled circles) and single-crystal (open squares) samples of LCMO. The inset shows the *M* versus *H* curves for the same samples.

of this superparamagnetic phase. The slope of this curve in the high field region for the single-crystal sample was nearly zero, whereas the magnetization of the porous sample gradually increased up to 5 T after rapidly increasing in the low field region. This suggests that a superparamagnetic phase exists in this porous sample. Another noteworthy feature in the $M(T)$ curve is that the Curie temperature (T_C) of the porous sample is much higher than that of the single crystal. One plausible explanation for the enhanced T_C is compositional fluctuation. Owing to selective gelation, the nominal composition of the product prepared by the sol—gel process can vary from the starting composition. So a high T_C phase in the perovskite $La_xCa_yMn_zO_{3+\delta}$ system may exist. Another possible cause is an oxygen annealing effect. The porous LCMO material can adsorb much more oxygen than the bulk material. Thus, oxygen saturation may lead to the enhanced T_C. In fact, a pronounced postannealing effect was observed in thin films of $La_{1-x}Ca_xMnO_3$ in which oxygen annealing increased the T_C up to room temperature.[11]

In summary, we have synthesized a porous LCMO material using PMMA spheres as a template. This porous network is composed of nanometer-sized LCMO wires with highly ordered spherical voids. An important feature is that the replicated magnetic pores with a 3D periodic structure exhibit both metallic and FM behavior. Preliminary experiments indicate that these pores can be filled with metals as well as various complex oxides, rendering new opportunities to create nanocomposites and hybrid materials with unique properties. Future work will also include investigating the magnetoresistive properties of the porous LCMO material, which is hampered by the brittleness of the sample.

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