Template assisted assembly of cobalt nanobowl arrays

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3-D interconnected networks of magnetic cobalt nanobowls with a wall size of <100 nm dimension have been fabricated. A novel technique was used to overcome the problem of volume shrinkage usually observed in such structures when formed by chemical conversion route. Cobalt particles were formed in the interstitial spaces of 3-D closed packed polystyrene (PS) colloidal template by borohydride reduction of a cobalt salt. Template removal was carried out by annealing either at 500 °C for 3 h in nitrogen or at 400 °C for 4 h in air, followed by toluene etching. The presence of an oxygen atmosphere during annealing was found to be imperative to obtain metallic cobalt. Magnetic measurements on cobalt nanobowl arrays showed enhanced coercivity in comparison to spherical particles due to shape effects.

Introduction

The colloidal crystal templated synthesis of nanostructured arrays has exhibited many potential applications in the areas of magnetics,1–6 photonics,7–10 biosensors,11 microchip reactors,12 photocatalysis,13,14 quantum electronics,13 lithium secondary batteries,15 magnetoelectric composites,16 and supports and carriers in chromatography.17 An ordered array of nanobowls in two dimensions has been shown to be useful for selecting spheres smaller than the inner diameter of the bowls,18 such bowls may also be useful for novel biomedical applications and nanofluidic devices. The shape dependence of magnetic properties at the nanoscale has generated interest in the fabrication of magnetic nanostructures of different shapes.1–6,19,20 Recently, three dimensional (3-D) ordered macroporous structures of ferromagnetic material which show unique magnetic properties have been fabricated using 3-D close packed arrays of monodisperse colloidal spheres as template.1–5,21 Yan et al.21 have reported the formation of 3-dimensionally ordered macroporous metal alloys of Ni2-xCo1-x (solid solution) and Mn5Co7 (an intermetallic compound) in which they employed the precipitation of mixed metal salts within the interstitials of a colloidal template of poly(methyl methacrylate) spheres. Bartlett et al.1 have pointed out the large volume shrinkage (up to 30%) and cracking of the material as disadvantages of this process. Since the precursor metal salts occupy a greater volume than the final alloy, such volume shrinkage was observed. Bartlett et al.1 instead used electrochemical deposition to fabricate macroporous structures of cobalt and nickel iron alloy without volume shrinkage. In many other reports the electodeposition technique has been used to form such nanostructures,4,5,8,15,22 however this greatly restricts the choice of materials and processing conditions.

Here we present a simple and versatile modified infiltration approach for the fabrication of 3-D cobalt nanobowl arrays by which volume shrinkage can be minimized. This new approach could widen the range of materials that can be processed as nanobowl arrays. In this process, cobalt nanobowls were formed by borohydride reduction of a cobalt salt in the interstitial spaces of a close packed polystyrene templates; this was followed by template removal by a combined sequence of annealing and toluene etching. The dependence of annealing temperature and atmosphere to achieve cobalt nanobowl arrays is presented. The coercivity value for Co nanobowl array was found to be greater than that for Co spherical particles due to shape effects.

Experimental

Formation of colloidal templates

In the fabrication process of the close packed colloidal template, monodisperse polystyrene latex microsphere suspensions with a mean diameter of 1.0 μm and a size distribution of 3% (Duke Scientific Corporation, USA) were used as received. The latex sphere suspensions were spun for 48 h at 800 rpm and air dried in the centrifuge tube to obtain centimeter-scale well-ordered close packed polymer templates. The template was strengthened by annealing at 100 °C for 10–15 min before infiltration of the void space.

Synthesis of nanobowl arrays

In a typical experiment to form nanobowl structures, 0.3 M cobalt chloride CoCl2·6H2O (LR/Resource) and 0.6 M sodium borohydride NaBH4 (Fluka) solutions were prepared in deionized water. First, CoCl2·6H2O solution was impregnated twice inside the interstitials of the close packed polystyrene (PS) template assisted by vacuum followed by NaBH4 solution which leads to the formation of cobalt particles in the interstitial spaces of the PS colloidal template. The template was dried for 24 h and the infiltration process was repeated in order to ensure complete filling of the interstitial spaces with cobalt particles. The infiltrated template was again dried for 24 h. All these steps were performed inside a N2 filled inert atmosphere glove box (Plas Labs, Lansing, USA) to prevent...
surface oxidation. The template was subsequently removed by annealing at 500 °C for 3 h in an N₂ atmosphere (set 1) and 400 °C for 4 h in an air atmosphere (set 2). After annealing, samples were washed in toluene and subsequently recovered from toluene using a permanent magnet.

Characterization

The morphology of the nanobowl network was investigated using a scanning electron microscope (SEM JSM-6360 or JSM-5410LV) operated at 15 kV or 20 kV. The samples were coated with a thin layer of gold using an SPI Supplies (USA) sputter coater and placed on conductive carbon tape adhered to an aluminium sample holder. Fourier transformation of the SEM micrographs was done using CRISP software. Powder X-ray diffraction (XRD) patterns of the nanobowls were collected using a Shimadzu 6000 Lab X diffractometer with Cu Kα radiation using step scanning in the 2θ range 10–80° at scanning rate of 0.02° s⁻¹. Quantitative phase analysis was conducted using the fundamental parameters Rietveld procedure as implemented in TOPAS R (version 2.1). For each refinement, the background parameter, scale factor, cell parameter, zero point correction and sample displacements were refined; however the atom positions, site occupancy factors, and isotropic thermal parameters were not. Magnetic measurements were carried out using a Lakeshore 736 vibrating sample magnetometer (VSM) at room temperature.

Results and discussion

Highly ordered interconnected nanobowl arrays were fabricated by using a colloidal template of 1 μm polystyrene spheres (Fig. 1). For the sample from set 1, after the vacuum assisted infiltration of the precursor materials in the interstitial spaces of the template, the polystyrene template was removed by a sequence of annealing (500 °C for 3 h in N₂ atmosphere) and toluene etching. This removal results in an ordered interconnected nanobowl array. Fig. 2(a) presents an SEM micrograph of the nanobowl array in a 60 μm x 45 μm region which shows the crystalline order of the network in distinct domains. This domain formation in the network is due to the presence of domains in the colloidal template, formed during the self-assembly of the polystyrene (PS) spheres. The Fourier transform of the selected region of Fig. 2(a) shows sharp peaks which confirm the crystalline order of network within distinct domains [Fig. 2(b)].

Previous literature had pointed out the disadvantages of the infiltration approach such as large volume shrinkage and cracking of the material. A smaller molar volume of the final material compared to the precursors could be the reason for the volume shrinkage. Since the synthesis step of metal formation inside the interstitials of the colloidal template includes heat treatment, competition between weight loss of PS spheres and metal formation takes place. This may be one more reason for the volume shrinkage and the presence of cracks observed by previous researchers. In our approach, a cobalt salt is chemically reduced inside the interstitial spaces of the colloidal template and filling of the interstitial spaces by the material is ensured by multiple infiltrations. Once the material is filled in the interstitials, it acquires the shape of a bowl and then annealing of the sample is carried out for template removal. Since annealing of the sample for template removal is done after the formation of the bowl structure by the material, the volume shrinkage is minimized as the average diameters of the bowls are ~1 μm [Fig. 2(c) and (d)] which is the same as the PS sphere diameter used in the template. The circular mouths of the bowls confirm that in this region, the thickness of the topmost layer is equal to the radius of the PS spheres used in the template. The walls of the bowl are of <100 nm dimensions. High magnification SEM micrographs [Fig. 2(c) and (d)], which show two distinct domains in the array, also show the interconnections within the network. In Fig. 2(c), point A is an example of an interconnection within the same layer while point B is an example of an interconnection with the underlayer. These interconnections are the point...
of contacts of spheres in the colloidal template, where the precursor material could not reach during infiltration, so no material formation occurs in those regions. The density of the sample was calculated using the SEM micrograph shown in Fig. 2(d). The average areal density of the dots formed in the interstitials was found to be $2.40 \times 10^8$ cm$^{-2}$ which is comparable to the expected density ($2.29 \times 10^8$ cm$^{-2}$).

Usually, template removal can be accomplished by either annealing the sample or by toluene etching, but in this work a combination of these two processes was employed. The advantage of this sequence is evident in Fig. 3(a) to (c). When the sample is annealed at 500 °C for 3 h in N$_2$ atmosphere [Fig. 3(a)], a considerable amount of PS residues can be observed in the micrograph due to incomplete burnout of PS spheres under inert atmosphere. The sample [Fig. 3(b)] which is only washed with toluene shows that material formation is not continuous inside the interstitials. The samples for which the template removal was carried out by a combined sequence of annealing and toluene etching shows continuous formation of cobalt inside the interstitials [Fig. 3(c)]. It is suggested that when we anneal the sample, interparticle bonding becomes stronger in order to reduce surface energy leading to formation of a continuous structure inside the interstitials. Annealing of the sample is also important to make the sample crystalline, because the as synthesized sample is amorphous [Fig. 4(A)]. In previous literature on similar types of structures but of binary and ternary oxides, it has been suggested that washing in a solvent is a better technique to remove the template,\textsuperscript{23} on the other hand in our case, a combination of annealing and washing with a solvent was essential for effective template removal as well as to make the material crystalline.

X-Ray diffraction patterns of the as synthesized sample and a sample which was annealed at 500 °C for 3 h in N$_2$ atmosphere (set 1) are provided in Fig. 4. The XRD pattern of the as synthesized sample (A), which was only etched with toluene and not annealed, shows that the material is amorphous while the XRD pattern of the set 1 sample (B) shows that it is comprised primarily of Co$_3$(BO$_3$)$_2$, Co(BO$_2$)$_2$ and Co$_3$B. The majority of the lines correspond to Co$_3$(BO$_3$)$_2$. This is because, during the synthesis, the formation of Co$_2$B (an intermediate) takes place which is subsequently converted into Co(BO$_2$)$_2$ after longer period (~15 min) of reaction. Upon heat treatment of this product, a solid state reaction converts Co(BO$_2$)$_2$ to Co$_3$(BO$_3$)$_2$. Additional XRD lines from Co$_3$B were also observed. This is because if some cobalt formation occurs during the reaction, it reacts with Co$_2$B to form Co$_3$B. The detailed mechanism of the formation of the Co$_2$B, Co(BO$_2$)$_2$ and Co$_3$(BO$_3$)$_2$ phases has been described elsewhere.\textsuperscript{24,25} For set 1, the Co$_3$(BO$_3$)$_2$ phase does not get converted to Co when annealed in N$_2$ atmosphere because of the absence of O$_2$. The magnetization curve of this sample is presented in Fig. 5. Low saturation magnetization (3.6 emu g$^{-1}$) and coercivity (15.9 Oe) of the sample were observed due to borate formation in the sample (Fig. 5).

Though, we achieved the morphology of set 1 in order to minimize the volume shrinkage, the nanobowls were composed...
of cobalt borate \( \text{Co}_3(\text{BO}_3)_2 \) instead of cobalt. So, to fabricate nanobowl arrays of metallic cobalt, another template was infiltrated with the same processing conditions as for set 1 except that for this set annealing was performed at 400 °C for 4 h in air atmosphere (set 2).

Fig. 6(a) shows a typical SEM micrograph of set 2, in which an ordered array of bowls with hexagonal mouths is shown. The non-circular (hexagonal) opening of the bowls indicates that the thickness of the topmost layer is greater than the radius of the bowl.1,9 A scheme of calculation of the diameter of the bowl has already been suggested,9 here we suggest a simpler scheme which is presented with the SEM micrograph. If we inscribe the hexagonal shape in a circle, the diameter of the circle can be used to obtain the bowl radius. From the SEM micrograph and geometrical calculations, the diameter of the bowl is estimated as \( y \) mm which is same as the diameter of the PS sphere in the template which shows that the volume shrinkage is minimized. The EDX spectrum [Fig. 6(b)] confirms the formation of cobalt and the absence of boron. Gold (Au) peaks are also observed in the spectrum because the SEM sample was prepared by sputtering of gold onto the sample.

The XRD pattern (Fig. 7) of the set 2 sample shows the absence of \( \text{Co}_3(\text{BO}_3)_2 \) contents in the sample and the presence of two distinct phases of cobalt. Thus we can see that, upon annealing the sample in air, \( \text{Co}_3(\text{BO}_3)_2 \) decomposes into metallic Co and \( \text{B}_2\text{O}_3 \).24,25 We believe that \( \text{B}_2\text{O}_3 \) thus formed remained in the toluene and cobalt is selectively recovered using a permanent magnet. To determine the percentage of each phase present in the sample, the XRD pattern was analyzed by Rietveld analysis (Fig. 7), which shows 68% of hexagonal cobalt (\( \varepsilon \)-phase)26 and 32% of fcc cobalt (\( \alpha \)-phase)27 is present in the sample. This is in accordance with the previous literature which describes that around 400 °C hcp cobalt starts converting into fcc cobalt.28 The crystallite size of the \( \varepsilon \)-cobalt is calculated to be 8 nm and that of the \( \alpha \)-cobalt is 35 nm. Though fcc Co is easy to oxidize, around 400 °C it is the stable phase.29

Magnetic measurements were carried out on the Co nanobowl arrays (set 2) and the magnetization curve is given in Fig. 8 which shows that the saturation magnetization of this sample is 57.6 emu g\(^{-1}\). The coercivity value of the set 2 sample was found to be 507.5 Oe which is higher than the coercivity of the spherical cobalt particles (375 Oe).30 Interestingly, the coercivity of set 2 is higher than the coercivity of the wire like structure (389 Oe) of the cobalt particles.30 This high coercivity value is possibly due to the shape anisotropy induced by the bowl structures in the sample. Since the network is interconnected, domain wall pinning due to the interconnections present in the array could be one more possible reason for the increased coercivity.1 The dependence of magnetic properties on the pore diameter of such types of structures synthesized by electrodeposition has been discussed previously by Zhukov et al.31,32 The synthesis of nanomagnetic hollow spheres by similar vacuum infiltration technique using 3-D PS colloidal template is ongoing.

**Fig. 6** (a) SEM micrograph of nanobowl array annealed at 400 °C for 4 h followed by toluene etching (set 2); a scheme for estimation of bowl diameter is also shown; (b) EDX spectrum of nanobowl array (set 2).
Conclusions

The synthesis and characterization of 3-D ordered cobalt nanobowl array were carried out by the infiltration of precursors in the interstitials of a colloidal template of PS spheres. The focus of the study was to investigate the effects of processing conditions on the morphology and structural properties of the material. The magnetic properties of the nanobowl arrays were also measured. The following conclusions were reached from the study:

1. A 3-D ordered interconnected array of cobalt nanobowls with the wall size of <100 nm dimension was synthesized with negligible volume shrinkage.
2. Synthesis of metallic cobalt was strongly dependent on the reaction conditions and annealing environment. The presence of oxygen in the annealing atmosphere is imperative to obtain metallic cobalt.
3. The magnetic measurement for the cobalt sample shows the effect of geometry and shape on coercivity. Induced shape anisotropy in the array increases the coercivity value.

References