

A novel method to synthesize cobalt (Co_3O_4) nanowires from cobalt (Co) nanobowls

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A novel method suitable for the synthesis of the cobalt oxide (Co_3O_4) nanowires at targeted regions is presented in this report. Cobalt (Co) nanobowls synthesized by colloidal crystal directed assembly were transformed into Co_3O_4 nanowires by a simple heat treatment process. Co nanobowls exhibited a two

phase (h.c.p. + f.c.c.) microstructure while single phase microstructure was observed for Co_3O_4 nanowires. Ferromagnetic Co nanobowls showed a dependence of coercivity on bowl size while Co_3O_4 exhibited weak ferromagnetic behavior.

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1 Introduction Cobalt (Co) and cobalt oxide (Co_3O_4) nanostructures are of great interest due to various advantages, e.g., Co nanobowls and nanowires exhibit interesting properties suitable for high density data storage and MRAM devices [1, 2], and can also be targeted at desired regions via an external magnetic field due to high magnetic moment while Co₃O₄ nanowires are extremely useful as anodes in batteries [3], catalysts, [4] and sensors [5]. Li et al. [3] have reported high capacity and rate capability of mesoporous Co₃O₄ nanowire arrays to be used as anodes in Li ion batteries. Recently, Xie et al. [4] have shown surprisingly high catalytic activity of Co₃O₄ nanorods. Co₃O₄ nanowires can also be used as electrochemical sensor for hydrogen peroxide sensing [5]. Increasing application of Co₃O₄ might also require the targeting of nanowires at particular regions in a device or system but Co_3O_4 is an anti-ferromagnetic material and exhibits zero net magnetization due to the complete compensation of sub-lattice magnetizations [6]. Targeting a material at a desired region can be carried out using an external magnetic field provided the material exhibits sufficiently high magnetic moment. Ferromagnetic behavior with a very small magnetic moment of Co₃O₄ nanostructures has been reported previously [7]; however it is impractical to process the nanostructures with such a weak magnetization using an external magnetic field. An alternative method of delivering Co₃O₄ nanowires is in situ synthesis at the desired regions. This can be achieved by

transforming Co nanostructures, which are well known to exhibit sufficiently high magnetization to be processed in an external magnetic field and can be targeted at desired regions, into Co_3O_4 nanowires.

This paper reports a novel strategy to convert Co nanobowls into Co_3O_4 nanowires by a simple heat treatment process in which Co nanobowls of 1 µm diameter, prepared by chemical synthesis technique incorporated within colloidal crystal templated assembly, were turned into Co_3O_4 nanowires upon annealing at 600 °C for 3 h. The formation of Co_3O_4 at high temperature annealing was due to the formation of unstable f.c.c. phase of Co. Magnetic properties of these Co nanobowls and Co_3O_4 nanowires were studied and presented. These nanobowls can also be used as nanocontainers for targeted delivery of useful liquids. This method has potential application for *in situ* synthesis of Co_3O_4 nanowires for systems and devices which can withstand up to 600 °C.

2 Experimental

2.1 Formation of colloidal templates Monodispersed polystyrene (PS) latex microsphere suspensions (particle density 1.05 g/cm^3 and a refractive index of 1.59 at 589 nm) with a mean diameter of $1.0 \,\mu\text{m}$ 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 followed by drying in a centrifuge tube to

a)

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.

2.2 Formation of nanobowls and nanowires In a typical experiment to form Co nanobowls [8], 0.3 M cobalt chloride (CoCl₂.6H₂O) (LR/Resource, APS Ajax Finechem, Australia) and 0.6 M sodium borohydride (NaBH₄) (Fluka, Milwaukee, WI) solutions were prepared in DI water. Vacuum-assisted infiltration was used to impregnate CoCl₂.6H₂O solution inside the interstitials of closed packed templates of PS spheres of 1 µm diameter. This was followed by impregnation of NaBH₄ solution leading to the formation of Co particles within the interstitial spaces of the PS colloidal template. All these steps were performed inside a N₂ filled dry box (Plas Labs, Lansing, MI). The template removal was carried out by annealing at 400 °C for 3 h in air followed by toluene etching. Co3O4 nanowires were prepared by the heat treatment of nanobowls at 600 $^\circ C$ for 3 h. The morphologies of the nanostructures were investigated using scanning electron microscopes (SEM) (JSM 5410LV and JSM-6360, JEOL, Japan) and a transmission electron microscope (TEM) (JEM-2010; JEOL, Japan). Powder X-ray diffraction (XRD) patterns were collected using a Shimadzu 6000 Lab X diffractometer (Japan) with CuKa radiation. XRD peaks were matched using Inorganic Crystal Structure Database (ICSD), Find It program. Magnetic measurements were carried out at room temperature using a Lakeshore 7404 (Westerville, OH) VSM.

3 Results and discussion In order to synthesize Co nanobowls, CoCl₂.6H₂O was chemically reduced within the interstitial spaces of the PS colloidal template by NaBH₄.

5 um



ď

200 nm

2 µm

Since the synthesis of the material takes place within the interstitials, it acquires the shape of a bowl. Removal of PS template was then carried out by annealing at 400 °C for 3 h in air which leaves Co nanobowls. Figures 1a and b presents the SEM micrograph of a close packed template of PS spheres and the Co nanobowls of 1 μ m diameter, respectively. The average wall size of the bowls was found to be 70 nm. Heat treatment of the nanobowls at 400 °C for longer duration (6 h) revealed a disrupted nanobowl structure (Fig. 1c) while heat treatment of the nanobowls at 600 °C for 3 h resulted in nanowires (Fig. 1d). High resolution SEM micrograph of a single nanowire is presented in the inset of Fig. 1d. The average diameter of nanowires was found to be 53 nm.

X-ray diffraction patterns collected on Co nanobowls are presented in Fig. 2. Interestingly, no oxide formation of Co was observed for the nanobowls samples obtained by annealing at 400 °C for 3 h in air, instead, a two-phase (h.c.p. + f.c.c.) microstructure of metallic Co was observed (Fig. 2a). The chemistry of borohydride reduction of CoCl₂.6H₂O leading to the formation of Co is as follows [8–10]; Co₂B and Co (BO₂)₂ are formed as the primary product (Eqs. (1)–(3)).

$$\begin{array}{l} 2\text{CoCl}_2 + 4\text{NaBH}_4 + 9\text{H}_2\text{O} \rightarrow \text{Co}_2\text{B} + 4\text{NaCl} \\ + 12.5\text{H}_2 + 3\text{B}(\text{OH})_3, \end{array} \tag{1}$$

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2O, \qquad (2)$$

$$Co^{2+} + 2NaBO_2 \rightarrow 2Na^+ + 2Co(BO_2)_2.$$
 (3)

The process by which Co is obtained is considered to be the pyrolysis of a mixture of Co_2B and $Co (BO_2)_2$ in air yielding Co and B_2O_3 (Eq. (4)). The other possibility is the



Figure 2 (online color at: www.pss-a.com) XRD pattern of Co nanobowls of 1 μ m diameter obtained by heat treatment at (a) 400 °C for 3 h, (b) 400 °C for 6 h. TEM micrograph of a single Co nanoparticle is presented in the inset.

sacrificial oxidation of Co_2B again yielding Co and B_2O_3 as the final product (Eq. (5)).

$$2Co_2B + Co(BO_2)_2 \rightarrow 5Co + 2B_2O_3,$$
 (4)

$$4\text{Co}_2\text{B} + 3\text{O}_2 \rightarrow 8\text{Co} + 2\text{B}_2\text{O}_3 \tag{5}$$

The removal of B_2O_3 (Eq. (4) and (5)) was carried out by washing the sample in DI water. The nanobowls heated at 400 °C for 6 h also shows the presence of same phases (h.c.p. and f.c.c.); no Co_3O_4 peaks were observed (Fig. 2b).

X-ray diffraction pattern of the Co nanobowls of 1 μ m diameter annealed at 600 °C for 3 h reveals the formation of Co₃O₄ nanowires (Fig. 3). The peaks observed in the XRD pattern can be indexed as (111), (220), (311), (400), (422), (511), (440), (620), and (533) planes of a cubic unit cell. The formation of f.c.c. phase at higher temperature is responsible for the oxidation of Co into Co₃O₄. It is well known that Co exhibits h.c.p. crystal structure (ϵ -phase) at room temperatures (>420 °C). The thermodynamics of Co at room temperature can be used to explain this phenomenon [11]. The free energy of formation of the cubic phase, starting from the hexagonal phase, is given by

$$\Delta G^{\varepsilon \to \alpha} = \Delta H^{\varepsilon \to \alpha} - T \Delta S^{\varepsilon \to \alpha} \tag{6}$$

where ΔG , ΔH , and ΔS , respectively, represents the free enthalpy, energy, and entropy of transformation from ε - to α -phase, and T is the temperature. For Co, $\Delta H^{\varepsilon \to \alpha}$ and $\Delta S^{\varepsilon \to \alpha}$ are positive, thus the enthalpy term favors the hexagonal phase while the entropy term opposes it. At room temperature, the enthalpy term dominates and the phase is hexagonal, while at higher temperatures (>420 °C) the entropy term dominates yielding the cubic phase. TEM micrograph of a single Co particle synthesized by similar borohydride reduction technique as used in this work (without using PS template) is provided in the inset of Fig. 2 which clearly reveals the presence of stacking faults. These stacking faults act as nuclei for this h.c.p. to f.c.c. phase transformation as the h.c.p. and f.c.c. structures differ only by the stacking sequence of close packed atomic layers (ABCABCABC for f.c.c. and ABABAB for h.c.p.). The f.c.c. structure of Co is less stable at room temperature and is more likely to oxidize in air and form Co₃O₄ [12]. Jahn-Teller distortion renders the h.c.p. structure more stable at room temperature than the f.c.c. structure [13]. This f.c.c. phase formed at higher temperature does not transform back to h.c.p. phase even after cooling the sample to room temperature. Oxide formation at high temperature annealing was responsible for nanowire formation as observed in SEM micrographs (Fig. 1d). The density of Co_3O_4 (6110 kg/m³, equivalent to a molar volume of $39.4 \times 10^{-6} \text{ m}^3/\text{mol}$) is significantly less than the density of Co (8900 kg/m^3) , equivalent to a molar volume of $6.6 \times 10^{-6} \text{ m}^3/\text{mol}$). The increase in molar volume of Co₃O₄ compared to Co (approximately sixfold) gives rise to large compressive stresses. In order to relieve these compressive stresses, protrusion of nanowires takes place as observed in Fig. 1d. It is noteworthy here that the nanobowls heated for 6 h were disrupted by diffusional processes [14] and no nanowires were observed (Fig. 1c) which confirms that the density change due to oxide formation is responsible for nanowire formation. A similar observation was made in the case of intermetallic formation in relation to Sn whiskers for microelectronics applications [15].

The magnetic hysteresis loops measured on Co nanobowls and Co_3O_4 nanowires are presented in Fig. 4. The saturation magnetization (M_s) and coercivity (H_c) values of Co nanobowls were found to be 57.6 emu/g and 507.5 Oe, respectively. The Co_3O_4 nanowires obtained by heat treatment of nanobowls showed a very small magnetic moment ($M_s \sim 0.3$ emu/g). Similar weak ferromagnetic



Figure 3 XRD pattern of Co_3O_4 nanowires obtained by heat treatment of Co nanobowls of 1 μ m diameter at 600 °C for 3 h.



Figure 4 (online color at: www.pss-a.com) Magnetic hysteresis loop measured on Co nanobowls and Co_3O_4 nanowires. Inset shows the magnified view of magnetization curve of Co_3O_4 nanowires.

behavior of Co_3O_4 has also been observed previously which was attributed to uncompensated surface spins and/or finite size effects or the partly inverted spinel structure [6].

4 Conclusions A technique to synthesize Co_3O_4 nanowires from ferromagnetic Co nanobowls was developed. This technique is useful for the synthesis of Co_3O_4 nanowires at desired regions. Co nanobowls were synthesized using colloidal crystal directed assembly process. These nanobowls were transformed into Co nanowires by high temperature annealing process. Co nanobowls exhibited the two phase (h.c.p. + f.c.c.) microstructure and strong ferromagnetic behavior while a single phase microstructure with weak ferromagnetic signal was obtained for Co_3O_4 nanowires.

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