MAGNETIC FIELD ASSISTED SYNTHESIS OF MAGNETIC NANOPARTICLES

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Abstract

A process for the production of magnetic nanoparticles having uniform size and shape in which a magnetic metallic substance selected from magnetic transitional metals, their alloys, and intermetallic alloys with non-magnetic metals, is dissolved in a non-aqueous medium, reacted with a reducing agent, in solution and the reaction mixture is subjected to an external magnetic field.
Figure 1
Figure 2
Co nanoparticles as-prepared

$600^\circ$C 1h with argon flow

JCPDS No. 15-0806

Figure 3
Figure 4
MAGNETIC FIELD ASSISTED SYNTHESIS OF MAGNETIC NANOPARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 60/603,477 filed Sep. 1, 2004, the content of which is incorporated herein by reference in its entirety.

GOVERNMENT LICENSE RIGHTS

[0002] The United States Government has rights in this invention as provided for by U.S. Defense Advanced Program Agency (DARPA) Grant No. F33615-01-2-2166.

BACKGROUND OF THE INVENTION

[0003] Magnetic nanoparticles are known to be very important in a wide variety of applications, such as ultrahigh density magnetic data storage, catalysts, drug delivery, cell separation, diagnostic, hyperthermia for cancer treatment, inductive bonding, ferrofluids and magnetic sensors. If such magnetic nanoparticles are to be used with the greatest effectiveness, it is crucial that they be produced with uniform size and shape and in a process that can be easily scaled up for large quantity production.

[0004] Existing techniques for the production of magnetic nanoparticles are problematic in that they are very costly, impractical for mass production or involve the use of undesirable toxic materials. For example, monodispersed nanoparticles of transition metals and their alloys may be produced by a polyol process, but it requires the use of expensive noble metals as seeds in order to obtain the desired small size.

[0005] Micro-emulsion or reverse micromulsion methods have produced acceptable magnetic nanocrystals but they are unsuitable for large quantity production.

[0006] Thermal decomposition methods are also known to produce magnetic nanoparticles but the organic metallic compounds used in this process, such as iron pentacarbonyl [Fe(CO)5], dicobalt octacarbonyl [Co2(CO)8] or nickel tetracarbonyl [Ni(CO)4], are expensive, unstable and very toxic. Thus, such methods are not conducive for large quantity production.

[0007] This invention avoids these problems and produces large quantities of uniformly-sized magnetic nanoparticles by controlling the growth of the emerging nanoparticles as they are formed through the use of an external magnetic field.

SUMMARY

[0008] In this invention, a novel process is provided for producing nanocrystals of uniform shape and size from magnetic transition metals, salts thereof, alloys of said metals and alloys of said metals with non-magnetic metals.

[0009] The process comprises essentially dissolving the selected magnetic transition metal, salt or alloy thereof in a non-aqueous solution and reducing the dissolved transition metal, salt or alloy in the presence of an external magnetic field.

[0010] In a preferred embodiment, borohydrides are employed as the reducing agent and the transition metal or alloy is dissolved in ethanol.

[0011] By performing the reduction reaction in a non-aqueous medium one is able to avoid the formation of transition metal borides which have much weaker ferromagnetism than pure transition metals and their alloys. By employing an external magnetic field in the reaction solution, one is able to control the nucleation, growth and size of the magnetic nanoparticles so as to achieve very uniform nanoparticles in large quantity. Any non-magnetic particles in the solution will not be attracted by the external magnetic field and may be separated out.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a schematic drawing of the experimental setup utilized in the example described herein.

[0013] FIG. 2 presents TEM graphs (a) and (b) show size distribution and shape and (c) to demonstrate selected area electron diffraction pattern.

[0014] FIG. 3 shows an XRD pattern of Co nanocrystals as-synthesized (red line) and subsequently annealed at 600°C. in Ar atmosphere for 1 hour (blue line). Vertical bars indicate the diffraction peak positions of fcc Co from JCPDS number 15-0806.

[0015] FIG. 4 is a hysteresis loop of as-synthesized Co nanocrystals (a, blue line) and subsequently annealed at 600°C. (b, blue line) for 1 hour and at 700°C. (b, red line) for 3 hours in H2 atmosphere.

DETAILED DESCRIPTION

[0016] The magnetic nanoparticles produced according to the process of this invention are formed from magnetic transition metals such as iron, cobalt and nickel, salts thereof, their alloys and intermetallic compounds such as CoP, CoFe, CoPt, CoPt3, Fe3Pt, FePt and FePt3.

[0017] It is important to this invention that the metals or their alloys which form the intended magnetic nanoparticles are reduced in a non-aqueous solution, preferably a lower alcohol such as methanol, ethanol, propanol, isopropanol and butanol. Ethanol is especially preferred.

[0018] Any of the known reducing agents may be used in the process of this invention, although a strong borohydride such as NaBH4 or KBH4 is preferred.

[0019] It is crucial to the formation of magnetic nanoparticles of uniform size and shape that the reaction solution be subjected to an external gradient magnetic field so as to adjust the dwelling time of the newly-formed magnetic nanoparticles in the reaction site, thus controlling their growth.

[0020] The materials produced by this invention may be used in exchanged coupled soft and hard magnets, ultrahigh density data storage media, catalysts, biological and medical applications such as cell separation, targetted drug delivery and hyperthermia treatment of tumors and infectious diseases.

EXAMPLE

[0021] CoCl2 and NaBH4 ethanol solutions were first prepared by dissolving appropriate amount of CoCl2 and NaBH4 into ethanol with vigorous stirring. The molar ration
of NaBH₄ over CoCl₂ was purposely made larger than 2 to ensure complete reduction of CoCl₂. The CoCl₂ ethanol solution was then put on top of a mineral oil layer which has a density larger than the above solution. NaBH₄ ethanol solution was added into CoCl₂ ethanol solution in a drop-like manner by using a dropping funnel or better using an ultrasonic atomizer that can give rise to small droplets of ~40 μm. According to Jackelen et al. [A. M. L. Jackelen, M Jungbauer, G. N. Glavee, Langmuir 1999, Vol. 15, PP 2322-2326], the following chemical reactions take place instantaneously when the NaBH₄ ethanol solution is added:

\[
\text{CoCl}_2 + 2\text{NaBH}_4 \rightarrow \text{Co} + \text{H}_2 + \text{B}_2\text{H}_6 + 2\text{NaCl}
\]

\[
\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \rightarrow 2\text{B}(	ext{OC}_2\text{H}_5)_3 + 6\text{H}_2
\]

[0022] The magnetic Co particles were attracted by a permanent magnet placed under the reaction beaker, which create a gradient magnetic field, (see FIG. 1) first into the interface between the oil and ethanol phases and finally into the oil phase. In this way, the particles are immediately taken away from the reaction site where BH₄⁻ ions are continually supplied. After the reaction was completed, the supernatant solution and the oil were discarded. The slurry were washed by ethanol, acetone and de-ionized water to thoroughly remove the residual oil and NaCl formed during the reaction, and finally washed by acetone again to remove water.

[0023] The resulting nanoparticles are shown in the drawing to have uniform size and shape. FIGS. 2a and b show the TEM graphs of the as-synthesized Co nanocrystals and confirm such a result. Very homogeneous particles with near perfect spherical shape are clearly seen in FIG. 2b, a histogram made using 250 randomly selected particles shows that the average particle size is around 4.7 nm with standard deviation of 1.6 nm. Since the as-prepared particles are small, the XRD pattern shows only a very broad peak [FIG. 3, bottom trace] corresponding to the diffraction line of face centered cubic (fcc) Co. After annealing the as-prepared particles at 600° C, for 1 h with argon flow, all diffraction lines of fcc Co appear but no Co—B alloy diffraction lines are detected [FIG. 3, upper trace]. In contrast to the present invention, this is usually found when the reduction is carried out in an aqueous solution. Therefore, by the method described here, one can fabricate pure Co nanoparticles. Although the XRD pattern for the as-prepared μCo nanoparticles lacks fine structure, the crystallinity was evidenced by the TEM associated electron diffraction pattern [FIG. 2(c)] indicating that the particles are well-crystallized fcc Co.

[0024] In FIG. 4(a), the M-H loop (solid triangles and line) for the as-prepared Co nanoparticles is plotted and measured at RT, showing typical superparamagnetic behavior. The magnetization curve can be fitted to a Langevin function with the summation of two size components [FIG. 4(a), dotted line; fitting parameters are indicated on the figure]

\[
M = M_1 \left[ \tanh (H/k_B T) - k_B T / \delta_1 \right] + M_2 \left[ \tanh (H/k_B T) - k_B T / \delta_2 \right]
\]

where \( M_1 \) and \( \mu_i \) (i=1, 2) are the saturation moment and the effective moments of a unit magnetic cell of each size component, respectively and \( k_B \) is the Boltzmann constant.

[0025] The TEMP graph shown in FIG. 2(b) indicates that the particles are almost perfectly spherical.

[0026] The zero-field cooled (solid triangles and dotted line) and 5 T-field cooled (solid circles and line) M-H loops (FIG. 4(b)) measured at 5 K nearly repeat each other, implying that the oxidation of particles were minimized.

[0027] While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

What is claimed is:

1. A process for producing magnetic nanoparticles of uniform shape and size comprising:
   a. forming a solution in a non-aqueous medium of a magnetic substance selected from the group consisting of magnetic transition metals, their salts and alloys and intermetallic alloys of said magnetic transition metals with non-magnetic metals;
   b. adding a reducing agent to the solution to form a reaction mixture, and c. applying an external gradient magnetic field to the reaction mixture.

2. A processing according to claim 1 in which the non-aqueous medium is a lower alcohol.

3. A process according to claim 2 in which the alcohol is ethanol.

4. A process according to claim 1 in which the reducing agent is a borohydride.

5. A process according to claim 3 in which the magnetic substance is cobalt.

6. A process according to claim 1 in which the magnetic substance is cobalt.

7. A process according to claim 1 in which the magnetic substance is a cobalt alloy with a non-magnetic metal.

8. A process according to claim 1 wherein the magnetic substance is an alloy of cobalt and another magnetic transition metal.

9. A process for producing magnetic nanoparticles of uniform size and shape comprising:
   a. dissolving a cobalt salt in ethanol;
   b. dissolving a borohydride compound in ethanol;
   c. adding the borohydride solution to the cobalt salt solution so as to cause a reduction reaction in the mixture;
   d. applying an external magnetic field to the reaction mixture.