Ionic Liquid Assisted Synthesis and Crystal Habit Control of Cobalt Accicular Nanoparticles

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ABSTRACT

We suggest a new method to synthesize well dispersed Cobalt (Co) acicular nanoparticles in water by a room temperature chemical reduction route. HRTEM images show that nanoparticles are needle shaped (acicular) with an average aspect ratio (length/diameter) between 3 and 13 when stabilizing agent tetramethyl ammonium hydroxide (TMAOH) is used to stabilize the particles. The aspect ratio depends upon precursor concentration, type of stabilization agent Tetra - (methyl, ethyl butyl) ammonium hydroxide added and inherent magnetic moment of the particles. Systematic experiments on cobalt suggest a plausible mechanism that involves oriented aggregation of initially formed spherical nanoparticles resulting in cobalt needles when TMAOH is used as structure directing agent. These needles grow normal to (100) plane that is assisted by cooperative role of cation TMA+ and anion OH-. The method is easily extended to nickel and iron oxide and synthesis of well formed acicular nanoparticles in these systems is demonstrated.

Introduction

Anisotropic nanoparticles of transition metals are of growing interest for scientific community. Synthesizing these nanoparticles with a tight control over size and shape distribution is often a challenge. Moreover, achieving size and shape control with water as a dispersion medium brings in greater complications. The synthesis of commonly encountered shapes, like rods, plates, cubes is studied in some depth, however, the truncated shapes like acicular (needles) particles, are not reported much. To bridge this, here we report a room temperature protocol for synthesis of water dispersed Co acicular nanoparticles. The protocol is based partly on seed mediated approach. It is worth mentioning that the growth of these particles is captured through high-resolution transmission electron microscopy (HRTEM) sliced down to short time intervals. The paper presents a detailed study of cobalt morphology control via stabilizing agent tetra-methyl ammonium hydroxide (TMAOH). Other systems are chosen to demonstrate the variation in morphology based on the stabilizing agent chosen and to assess impact of various controlled experimental parameters.

Co, Ni and Fe find wide applications in field of catalysis, biomedical science and electronics [1-3]. Occurrence of shape anisotropy in these particles enhances their highly sought property of magnetism, which is size and shape dependent phenomenon. Through a tight control on shape and size distribution desired physicochemical properties can be achieved via chemical reduction route, thus, increasing possibility to explore new applications with these particles. Various methods are already reported for controlled synthesis of magnetic nanoparticles like, thermal decomposition, sol-gel method, templating against alumina pores [4-6] etc. Using ionic liquids for shape and size control is rather a new technique [7] favouring in-situ synthesis of magnetic nanoparticles with water as a reaction and dispersion medium rendering an excellent yield and shape control over nanoparticles. Such method eliminates relatively tedious technique of phase transferring the particles from oil to water. Ionic liquids are characterized by their melting point below room temperature and a very high ionic concentration of either of the counterion. They represent asymmetric class of stabilization agents which facilitate anisotropic growth [7].
Materials and Methods

Materials

Cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O), stabilizing agent tetra-methyl-ammonium hydroxide (TMAOH, 25% w/w aqueous) were procured from Merck Chemicals and Fluka (Sigma-Aldrich) India. All other reagents, such as sodium borohydride (NaBH$_4$), tetra-butyl-ammonium hydroxide (TBAOH) were obtained from Merck Chemicals (India). In all the experiments MilliQ water of conductivity 18.2 M Ω cm$^{-1}$ was used and the temperature was maintained at 27°C unless otherwise mentioned.

Methods

Synthesis of Cobalt Nanoparticles

A three step protocol is followed for producing Co nanoneedles. A typical synthesis involves direct reduction of the cobalt precursor (0.8 mL of 0.4M solution) by sodium borohydride (100 mL of 0.01M made in deaerated MilliQ water) to form seed particles. The reaction was carried out under ultrasonication and the resulting black precipitate was collected using a strong permanent magnet. The precipitate was further washed, at least four times, with MilliQ water, to remove traces of unreacted species. The black precipitate formed the seed particles of thus formed. A molarity of 0.4M cobalt and 0.01M borohydride was scanned to optimize the size of cobalt nanocluster. A concentration ratio of cobalt ions to hydroxide (TMAOH) or TBAOH particles of thus formed. A molarity of 0.4M cobalt and 0.01M borohydride was scanned to optimize the size of cobalt nanocluster. A concentration ratio of cobalt ions to hydroxide (TMAOH) or TBAOH

Studies were performed to optimize the seed particle size of cobalt nanocluster. A concentration ratio of cobalt ions to borohydride was scanned to optimize the size of cobalt seed particles of thus formed. A molarity of 0.4M cobalt and 0.01M NaBH$_4$ yielded seed particles of size from 15-30 nm (Fig.1) to which the TMAOH of 2.7M when added resulted in a good yield of well formed anisotropic nanoneedles. Keeping the seed particle size and stabilizing agent molarity same as mentioned above, time evolution of acicular nanoneedles was observed through high-resolution transmission electron microscopy (HRTEM). Maintaining same concentration values, TMAOH was then replaced by TBAOH, to study the effect change on the shape. Other experimental conditions were kept constant. A detailed discussion is presented in subsequent section.

Characterization

The kinetics of formation of Co nano-needles and other aspects was investigated by the size and shape analysis of HRTEM images of the sample, taken at various time intervals. HRTEM investigations were carried out using (JEM 2100F field emission machine, 200kV). A small drop of a sample was placed on a carbon coated copper grid and vacuum dried at room temperature for around 12 hours. The images were taken at different magnifications to understand the morphology and crystal habit of the nanoparticles. For the same samples, energy dispersive spectrum (EDS) graphs of respective samples were obtained to confirm the native state of nanoparticles and also to detect traces of other reactant species.

The zeta potential studies were performed on Dynamic Light Scattering (DLS Zetasizer Nano ZS Malvern Instruments, UK) at 25 °C. The X-Ray Diffraction (XRD) measurements of all the nanoparticles were carried out on a Rigaku D-max 2000/JADE 6.0 copper rotating anode X-Ray Diffractometer using Cu-k$\alpha_1$ radiation. The magnetic properties of samples were determined by Quantum Design Vibrating Sample Magnetometer (Quantum Design, USA) at room temperature (at 300K).

Results

Cobalt Accicular Nanoparticles—Growth Regime

Shape evolution with time for Co-seeds treated with TMAOH was traced using HRTEM. As shown in images (Fig.3), particles at zero minutes are spherical and possess twinned surface. The size is around 30 nm. At 15 minutes, the particles size drops down to 8-15 nm. The particles are still spherical and the tendency for aggregation here can clearly be identified. The micrograph in Fig 3 (10 and 15 minutes) supports the 1-
dimensional aggregation. The aggregation and consolidation of the intermediate structures continues with subsequent aging of the growth solution. Anisotropy in the system first appears at 30 minutes with well formed acicular needles; these particles further grow and attain stable shape and size with average length of 295±14 nm and diameter of 30±2 nm around 120 minutes. Fig.4 shows the change in diameter, length and aspect ratio (AR) with time of nano-needles. The average diameter obtained at 15 minutes is smaller than as obtained at zero minutes. The size reduction is possibly due to the de-clustering of initially twinned spherical nanoparticles followed by their rearrangement in presence of stabilization agent.

The tendency of aggregation can be justified by continuous Brownian motion of nanoparticles and their inherent magnetism. These particles are likely to magnetize and attract surrounding nanocrystals through dipolar interaction leading to 1-dimensional self-assembly [8].

Experimental observations indicate that the growth and shape of anisotropic nanoparticles is largely controlled by dynamic factors such as, presence of optimum concentration of OH⁻ anion, presence of pre-formed seed particles, molarity of the stabilizing agent, associated magnetic moment of particles and their collision frequency. These dynamic parameters were investigated independently to develop a synergistic approach to obtain nano-needles.

To verify the role of magnetic moment, in a similar protocol as explained in previous section, Co was replaced by zinc, which is diamagnetic in nature. Addition of TMAOH to initially prepared Zn spherical nanoparticles seeds did not show anisotropy when observed at 15 and 45 minutes measured after ultrasonication (size remains constant ~ 15 nm). Therefore, the role of magnetic moment is emphasized.

Hydroxide (OH⁻) anion in an optimum concentration was crucial for formation of anisotropic shapes. The alkyl group is also important. To understand role of alkyl group, in an experiment TBAOH was used instead of TMAOH for stabilization. An inhibitory growth effect was observed for Co-TBAOH nanoparticles (Fig.6). The micrographs in Fig. 5 show that the particles are nearly spherical and randomly aggregated.
The reduction in size in the case of TBAOH is a combined effect of bulkier alkyl group and lesser dissociation of OH⁻. The bulkier cationic group in TBAOH, due stearic hindrance prevents the assembly of spherical nanoparticles and lesser availability of OH⁻ alters the surface interactions at cobalt seeds. This marked difference in morphologies for TMAOH and TBAOH is therefore, because of different cation groups and different degree of dissociation of OH⁻ anion from respective cation.

An effective role of OH⁻ is well cited in literature [10] through surface absorption, tailoring the electrode potentials and nucleation and growth rates. In the present study, OH⁻ through TMAOH is added only after the completion of reduction reaction. However, it is speculated that directed attachment of monomers of Co is controlled by ionic concentration of OH⁻. OH⁻ anion is observed to be essential for formation of non-spherical nanoparticles. Experiments conducted using other stabilization agents such as ammonium hydroxide and tetra-ethyl-ammonium hydroxides yield spindle and smaller size rods, respectively. Thus, they substantiate that the anisotropy is generated by presence of OH⁻ and alkyl group. The series of tetraalkyl ammonium ions (RN⁺) (symmetrical n-alkyl-methyl, ethyl, and butyl) represent a class of apolar systems their hydrophobicity increases with increasing alkyl radius. The atomic radius of cations varies as 2.79 Å, 3.36 Å, and 3.78 Å respectively for methyl, ethyl and butyl groups. For NH₄⁺ radius of gyration is reported as 0.90 Å [9]. Increasing the atomic radii, due to stearic hindrance, restricts the monomer addition required for anisotropy generation. This forms compact structures with increased sphericity as we vary stabilization agent from methyl, ethyl, and butyl.

Cobalt Crystal Habit

Nanoparticles typically have a reduced domain size or crystallite size that can lead to broad peaks. The Co-nanoneedles obtained in case of TMAOH showed diffraction peaks for hcp crystal habit. The XRD spectrum is shown in Fig.7. Analysis of the XRD spectrum shows sharp peaks and presence of hcp crystal phase for cobalt. The crystal planes in sample are identified as: 2.22 Å ~ 100 hcp, 2.03 Å ~ 002 hcp, 1.76 Å ~ 200 hcp, and 1.25 Å ~ 110 hcp.

The high resolution image (Fig.8) show 0.22 nm planar spacing, which belong to [100] planes of hcp cobalt, this suggests that TMA⁺ restrict [100] plane so that the needles grow only in the direction normal to the [100] plane (Fig.9). The lowest intensity of [100] planes in XRD supports this HRTEM observation.

In summary, changing the stabilization agent leads to formation of different shapes in nanocrystals. TMAOH shows high affinity for certain planes of Co crystals.

Figure 6: Co-TBAOH nanoparticles, (A) – image captured at 15 minutes ageing time, (B) – image captured at 45 minutes ageing time. Nearly spherical nanoparticles are observed at both the time intervals unlike anisotropic shapes for Co-TMAOH.

Figure 7: XRD Spectrum of Co-TMAOH. XRD sample take at end of the sample ageing (120 minutes), evolution of peaks can be observed after heat treating the sample.
For present case, magnetization studies of Co-needles were performed at the end of their growth curve (~ 120 minutes). The saturation magnetization \(M_s\) and coercivity \(H_c\) values for Co-TMAOH needles were found to be \(\sim 10\) emu/g and 400 Oe respectively (Fig.9). It was observed that the presence of stabilizing agent on the surface of needles greatly affects the value of saturation magnetization. Increase in \(M_s\) is observed after removal of TMAOH (\(\sim 30\) emu/gm). However, no significant change is observed in the value of coercivity of the system. With longitudinal direction as the easy (preferred) direction of magnetization it can be observed that the Co-needle saturate faster when compared to spherical Co nanoparticles which have \(M_s = 35\) emu/gm (figure not shown here). With an added longitudinal axis, the shape anisotropy is observed for elongated nanoparticles. Considering anisotropy in magnetic nanoparticles, eg acicular (needle shape) nanoparticles they are more easily susceptible for magnetic texturing i.e ordering of directions of magnetic axes of the particles and the preferred axis is longitudinal [10]. The smaller value of \(M_s\) of for our particles is justified due to spin disorder on the surface arising due to reduced surface area [10].

### Conclusion

Ionic liquid based stabilizing agents, \(tetraalkylammonium\) hydroxides are tested and optimized to yield shape and size controlled nanoparticles of cobalt. The morphology changes from acicular to spherical, depending on the type of counterion on the stabilizing agent molecule. It is concluded that the ionic liquids TMAOH yield anisotropic nanoparticles as equilibrium shapes for which the presence of OH\textsuperscript{-} ions is essential. Also with bulkier alkyl group more compact and spherical structures are generated. HRTEM images reveal that the anisotropic shapes are an outcome of agglomeration of spherical nanoparticles which is supported by magnetic moment, particle-particle collision and influenced and directed by selective affinity of stabilizing legand (TMA\textsuperscript{+}, and TBA\textsuperscript{+}). Selective affinity of counterion legand propels the growth in different directions for nanocrystals and modulates the equilibrium shape as well. Magnetic properties of needles are significantly affected because of shape anisotropy.

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### References


