Synthesis and Characterization of Monodisperse Cobalt Nanocrystals and Nanocrystalline Superlattices

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Synthesis and Characterization of Monodisperse Cobalt Nanocrystals and Nanocrystalline Superlattices

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Abstract  Magnetic colloids of cobalt nanocrystals (NCs) were prepared by reducing solute cobalt chloride in the presence of stabilizing agents at a high temperature. The nanocrystalline samples were nearly monodisperse with narrow size distribution of about 7%. X-ray diffraction result showed that Co NCs had a third distinct crystal structure related to the beta phase of manganese. A red shift of the maximum absorption peak of the UV-visible spectra occurred with the increasing diameter of particles, which indicated that we could coarsely control average particle size by adjusting the concentration ratio of cobalt to surfactants. The size of these NCs samples was uniform enough to self-assemble into close-packed and ordered NCs superlattices.

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1. INTRODUCTION

Nanocrystals (NCs) of nanometer size are a new generation of advanced materials exhibiting both chemical and physical properties which are different from those of the bulk materials and the single atoms. Materials with nanometer size have unusual electronic, magnetic, optical, and structural properties. Magnetic colloids and ferrofluids have been studied to explore the dependence of the fundamental properties on the size of magnetic particles. And the attempts on their applications have been intensively made. The desire to identify and understand the size-dependent properties of materials at the nanometer scale has motivated the preparation of size-tunable monodisperse nanoparticles with controllable internal structures. For example, magnetic[1] and semiconducting[2] NCs exhibit strong size-dependent properties that may provide insight into the scale limits of magnetic storage and microelectronics, which are crucial to information technology. The preparation of NCs samples that are uniform in composition, size, shape, internal structures and surface chemical properties is crucial to successfully mapping their size-dependent properties. High-temperature, solution-phase reducing method provides us a way to synthesize monodisperse cobalt NCs[3]. This method is based on rapidly adding reagents into a hot and homogenous solvent, which can provide temporary discrete nucleation and allow us to control the growth of nanocrystals[4]. When the NCs samples reach the desired size, further growth can be stopped by cooling the solution. Each NC has an inorganic crystalline core, which is surrounded by an organic monolayer that prevents oxidation and irreversible aggregation of the particles.
Solution phase chemical synthesis is generally not thermodynamically controlled, which makes it possible to prepare metastable crystal phases\(^5\).

In this article, we describe the reduction of cobalt chloride with lithium triethyl boronhydride (superhydride) to produce cobalt nanoparticles with cubic symmetry of the \(\beta\) phase of manganese which is distinct from the symmetries of the fcc and hcp forms. In our experiment, the surfactant, triphenylphosphine was used to control the size of Co nanocrystals, because it has great steric hindrance and it is cheaper. Different molar ratios of Co/surfactants were employed to produce nanoparticles with different sizes. The structure and superlattices of Co nanocrystals were characterized by XRD and TEM respectively.

2. EXPERIMENT

2.1 Materials The experiment of synthesis was carried out under nitrogen purge. All reagents were purchased from ACROS. Diphenylether solution of superhydride (LiBE\(_3\)H) was prepared by first mixing the tetrahydrofuran (THF) superhydride solution with diphenylether and then evaporating THF.

2.2 Nanocrystal Synthesis 0.13g cobalt chloride (anhydrous), 0.32ml oleic acid (octadec-9-ene-1-carboxylic acid, CH\(_2\)(CH\(_2\))\(_5\)CH=CH(CH\(_2\))\(_7\)COOH) and diphenylether (30ml) were mixed together under nitrogen and then heated nearly to 100\(^\circ\)C. Then 0.79g triphenylphosphine (PPH\(_3\)) was added and heated to \(\sim\)210\(^\circ\)C. The Co nanoparticles began to emerge with the injection of (2ml) diphenylether
superhydride during vigorously stirring solution. The color gradually changed from blue to black during the first minute as the Co NCs nucleated and began to grow. The reaction was held at \( \sim 200^\circ C \) for 30min. Then the dispersion Co NCs was cooled down to room temperature. Particles were precipitated by adding ethanol into the system. The supernatant was discarded by centrifugation, and the precipitates were again dispersed in 15ml heptane with a drop of oleic acid to ensure the stability of nanoparticles. This preparation yielded Co NCs with a size distribution about 7%.

2.3 Size-selection and Self-assembly Size-selective precipitation involved adding a nonsolvent miscible solution into the original system drop by drop to bring about its slight cloudiness. Since the largest NCs had the greatest attractive forces, they aggregated first. So by centrifuging, precipitates rich in the largest NCs were attained. The supernatant solution, containing the majority of the NCs, was then decanted, and more nonsolvent was added drop by drop until a dense, cloudy suspension appeared. Centrifuging isolated most of the NCs in the precipitates, leaving the smallest NCs and synthetic by-products in the supernatant solution, which were then discarded. Repeating the procedure, the size distribution was further narrowed, and a series of nearly monodisperse NCs were produced.

Self-assembly of colloid NCs was formed by evaporating the heptane from the dispersion on a copper grid coated by carbon film at room temperature, and then covering the solution/substrate with a petridish to slow down the evaporating rate.
Besides the requirement on the narrow size distribution of samples, the character of dispersing solvent and the temperature during deposition were also crucial to achieving the long-range order in assembly of NCs. The dispersing solvent with the required boiling point was selected to slow the evaporation rate and thus to give the NCs enough time to find energetically favorable sites of lattices in a growing assembly\cite{6}. The solvent used to deposit the NCs superlattices was selected according to its polarity and boiling point. The preferred solvent polarity was chosen so that the interaction between NCs would become mildly attractive as the solvent was evaporated and the dispersion became more concentrated. In this experiment, we used heptane as dispersing solvent. The formation of superlattices is driven by attractive van der waals forces and magnetic interactions between the particles.

2.4 Characterization of Samples The structure of Co nanocrystals was investigated by a Rigaku D/MAX-200 x-ray diffractometer with Cu Kα radiation (λ =1.5406Å). UV-visible absorption spectra of nanocrystals dispersions in heptane were measured using a Shimadzu UV-1601 PC double beam spectrophotometer. The graphs of transmission electron microscopy (TEM) were obtained from JEM 200CX and CM 200FEG operating at 200KV. The samples for TEM analysis were prepared by depositing one drop of heptane dispersion of cobalt particles onto a copper grid coated by carbon film, followed by naturally evaporating solution.
3. RESULTS AND DISCUSSION

3.1 Structural Analysis There are only two stable crystal phases known for elemental cobalt at normal pressure. The bulk hcp is stable at temperature below 425°C, while the bulk fcc is the stable structure at a higher temperature. Here the crystal phase of the cobalt Ncs is neither fcc nor hcp. Fig. 1 shows the diffraction patterns of Co nanocrystals, indicating a crystal structure with the symmetry found in the β phase of an elemental Mn. This crystal structure has been designated as the $\varepsilon$ phase of cobalt ($\varepsilon$-Co). The X-ray diffraction curve has three peaks at $2\theta=49.580$, 56.320 and 80.340, corresponding to the (221), (310) and (311) plan of the $\varepsilon$-Co lattices respectively. It is shown that as molar ratio of Co/surfactant (triphosphine) gradually increases, the shapes of diffraction peaks become sharper and the intensity stronger. This demonstrates that the size of Co NCs is increasing in the process. The fact above proves that the size of Co nanocrystals can be controlled by changing the molar ratio of the Co/surfactant.

3.2 The Size of Co NCs The systematic adjustment of reaction conditions –time, temperature, concentrations of reagents and surfactants can be used to control NCs size and thus to prepare a series of NCs samples with different sizes. In general, the size of the NCs increases in the experiment with increasing reaction time, some more materials are added to the NCs surfaces. Increasing temperature will also cause the growth. Moreover, adjusting the concentration ratio of reagents to surfactants provides another control over NCs size, because high stabilizer-to-reactant
concentrations favor smaller nuclei initially and thus a smaller NC size\cite{7}. Chemical properties of surface agent can influence NCs size as well during their growth, for surfactants in solution are absorbed reversibly to the surfaces of the NCs, providing a dynamic organic shell that can stabilize the NCs in solution and mediate their growth. An effective strategy is using a pair of surface agents. One of them is tightly bound to the NCs surface to provide greater steric hindrance to slow the growth rate, and the other is weakly bound, permitting rapid growth\cite{5}. In this experiment, properly adjusting of the concentration ratio of oleic acid (tightly bound) to triphenylphosphine (weakly bound) can control the growth rate, and in return the size of NCs.

3.3 Optical Characterization The size of cobalt nanoparticles was traced by the UV-visible absorption method. Fig. 2 shows the peak positions and the shapes of the absorption spectra of nanoparticles with different sizes. When the concentration ratio of triphenylphosphine stabilizer to cobalt increases, the red shift of the maximum absorption peak occurs, which indicates the diameter of particles increases. By this method, we can coarsely control the average size of particles.

3.4 The Self-assembly of Co Nanoparticles Fig. 3 shows the TEM image of Co nanocrystals. Within the TEM image, cobalt nanoparticles with 9nm mean diameter are nearly monodisperse. Every particle is separated from its neighbors by the surfactants. In the inset, the ε-Co nanocrystals are uniform in both size and shape, which makes it possible for them to self-assemble into a two-dimensional
monodisperse film. We can observe that the distance between two particles is 2nm, nearly the length of the surfactant molecules. The upper inset is the 2D Fourier transform power spectrum of the zoomed area, which demonstrates that the superlattice of the ordered nanoparticles is of a hexagonal closed-packed (hcp) structure. High-resolution TEM image in Fig. 4 shows a projection of a superlattice formed from 9-nm Co NCs.

4. CONCLUSIONS

Monodisperse cobalt NCs with β-Mn phase have been prepared employing high temperature, solution phase reduction. By adjusting the concentration ratio of oleic acid to triphenylphosphine stabilizers, the size of cobalt nanoparticles can be controlled. The long-range order of close-packed nanoparticle arrays, as confirmed by TEM, was obtained by self-assembly.
REFERENCES


Figure Captions

FIG 1. XRD patterns of Co nanocrystals at different concentration ratios of oleic acid to triphenylphosphine, a=1:3, b=1:5, c=1:7.

FIG 2. UV-vis spectra of the Co nanocrystals at different concentration ratios of oleic acid to triphenylphosphine, a=1:3, b=1:5, c=1:7.

FIG 3. TEM image of two-dimensional superlattice Co nanocrystals of 9nm; The upper inset is the 2D Fourier transform power spectrum of the TEM image and the lower inset shows highly ordered Co nanoparticles in selected area.

FIG 4. High-resolution TEM image of a superlattice of 9-nm Co NCs, showing the twin structure of the order Co nanoparticles.
Figure 1

(Y. K. Su, et al. submitted)
Figure 2

(Y. K. Su, et al. submitted)
Figure 3

(Y. K. Su, et al. submitted)
Figure 4

(Y. K. Su, et al. submitted)