A general approach to synthesis of nanoparticles with controlled morphologies and magnetic properties

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We present a systematic approach to fabricate a variety of magnetic nanoparticles with desirable structure and controlled magnetic properties based on our studies of the process kinetics. The morphology of binary alloy particles is dependent on their bulk thermodynamics—for immiscible heterogeneous systems (Co–Au) core-shell structures are obtained while miscible systems (Fe–Pt) lead to alloy nanoparticles. The annealing effects on FePt nanoparticles show that the coercivity and magnetic anisotropy increase dramatically after annealing at temperatures above 650 °C. Studies of Co–Au core-shell structure show that the core is magnetic, but the Au shell does not significantly affect its magnetic properties. © 2005 American Institute of Physics. [DOI: 10.1063/1.1853991]

I. INTRODUCTION

Chemical solution methods have been widely used to produce nanostructured materials, and different strategies have been applied to achieve monodisperse nanoparticles with controlled size and shape. However, there is no general strategy to make nanoparticles with narrow size distribution, tailored properties, and desired morphologies, which could be universally applied to different materials. It is believed that nanoparticle formation follows the classic LaMer mechanism, which suggests a short burst of nucleation followed by slow diffusive growth, favoring formation of monodisperse crystalline nanoparticles. Our experience shows that the synthesis is a multiplet-step process, which provides us the capability of producing controlled morphology single and binary alloy nanoparticles by separating the nucleation and particle growth stage during synthesis.

In this paper, we suggest a general approach for the fabrication of magnetic nanoparticles with desired composition, structure, morphology, and properties. Systematic studies have been performed on cobalt particles as a model system. We demonstrate formation of single crystalline or multiple-grained particles with controlled defects and discuss the formation and growth mechanisms. This knowledge is used in the fabrication of more complex systems for different applications. In particular, biocompatible air-stable gold-coated cobalt core-shell nanoparticles and hard magnetic alloy nanoparticles (FePt) can be synthesized. In these cases annealing effects are also studied as an integral part of the process leading to special crystal structures and geometries.

II. SYNTHESIS STRATEGY

We first consider the possible reaction routes leading to the formation of either single crystalline or multiple-grained cobalt nanoparticles in the reaction involving decomposition of cobalt carbonyl.2,3 At the beginning of the synthesis, a supersaturated solution of cobalt is formed by the decomposition of cobalt carbonyl, leading to the nucleation of the nanoparticles. However, further particle growth is strongly dependent on the available monomer concentration and the existing surfactants in the system. The nuclei may then either grow by a diffusive mechanism or by aggregation. For very high monomer concentration in solution, the nuclei grow in the high chemical potential environment to form single crystalline nanoparticles (LaMer mechanism); however, if the monomer concentration is relatively low, the monomer concentration will be quickly depleted. This results in the formation of small primary particles, which then aggregate to form the final size particles.4 As a result of this process, known as aggregation of subunits, multiple-grained nanoparticles are synthesized.

As a synthesis strategy, separation of the nucleation and particle growth in the solution can be extended to other materials system as well. When the nuclei are of different elements, binary particles can be easily achieved. The morphology of binary particles is dependent on the miscibility of the materials. For immiscible heterogeneous systems such as Co–Au, core-shell structures are obtained, while miscible systems (Fe–Pt) lead to alloy nanoparticles.

III. EXAMPLES OF NANOPARTICLES AND THEIR PROPERTIES

A. Cobalt nanoparticles

Cobalt nanoparticles were synthesized by rapid decomposition of organometallic precursors in a coordinated solvent containing different surfactants in an argon atmosphere. All the chemicals were obtained from commercial sources and used without further purification. Cobalt carbonyl [1.58 mmol (0.54 g)] dissolved in 3 ml 1,2-dichlorobenzene (DCB) was injected into DCB (182 °C) containing a mixture of 0.6 mmol (0.2 ml) oleic acid and 1.1 mmol (0.34 ml) dioctylamine and refluxed for 15 min. Crystal structure was studied with x-ray diffraction (XRD) and transmission electron microscopy (TEM). TEM samples were prepared by...
evaporating the solvent from a drop of the particle solution on a TEM grid. TEM images of 10 nm cobalt nanocrystal are shown in Figs. 1(a) and 1(b) TEM image shows that the cobalt nanoparticles are spherical with narrow size distribution. However, both the dark field image and the high-resolution TEM images suggest that the nanoparticles comprise multiple crystal grains with clear grain boundaries. XRD samples were prepared by precipitating the particles with methanol, a nonsolvent, into powder form. Both the peak position and the relative peak intensity of $\theta-2\theta$ scan suggest that the cobalt nanocrystals are $\varepsilon$-cobalt$^5$ [Fig. 2(a)].

Magnetic properties of these powder form samples were investigated with superconducting quantum interference device. The zero field cooled (ZFC) magnetization measurement shows that the particles are superparamagnetic at room temperature, with the blocking temperature about 220 K. The blocking peak also suggests a relative narrow size distribution of these nanoparticles [Fig. 2(b)]. However, the surface stability against oxidation is different for multiple-grained nanoparticles, compared to single crystalline cobalt nanoparticles.$^3$

**B. Co–Au core-shell nanoparticles**

The process can be modified to use premade nanoparticles as nuclei. In particular, this route is useful in the synthesis of core-shell structures. By using premade $\varepsilon$-cobalt nanoparticles as nuclei and Au compounds as a monomer, we can grow core-shell Au-coated Co nanoparticles. Cobalt seed solution [0.5 ml (3 mmol/ml)] was mixed together with 5 ml toluene, degassing with argon flow for at least 30 min, then a solution of 0.01 g HAuCl$_4$, 0.25 ml oleylamine, and 3 ml toluene was injected into solution at 85 °C. After the reaction, the solution was kept at this temperature for 1 h; a core-shell structure with about 6 nm core and 1.5 nm shell was formed. The sizes are directly measured from the TEM images [Fig. 1(c)]. TEM contrast depends on the mass thickness of the samples with heavier elements appearing darker than the lighter elements. The contrast variation from the core to the shell suggests that the Au shell is formed around the cobalt core. The x-ray diffraction pattern [Fig. 3(a)] shows only peaks corresponding to the fcc metallic gold
structure. The cobalt peaks are not clearly resolved, probably due to peak broadening and the difficulty to detect cobalt from gold.

The particles are ferromagnetic at 5 K [Fig. 3(b) inset], indicating the presence of cobalt cores. The ZFC-FC measurements show a narrow peak at about 55 K, suggesting magnetic size of the core-shell particles is narrow. Since the blocking peak is only related to the magnetic volume, the 55 K blocking peak indicates that the core size is about 5–6 nm, which agrees with the size measured from the TEM images. This is an approximate estimate based on comparison with similar measurements on several pure Co nanoparticle powders of different diameters in the range 5–15 nm. This core-shell system may find a number of biomedical applications because of the strong magnetic signal, biocompatibility, and the well-studied gold chemistry that leads to a wide range of surface modification strategies.

C. FePt nanoparticles

FePt nanoparticles were synthesized by a modified form of the method reported by Sun et al.\textsuperscript{6} 0.05 ml Fe(CO)\textsubscript{5} was injected into 10 ml phenyl ether in the present of 0.08 ml oleic acid at 180 °C under argon atmosphere. The solution was kept at this temperature for half an hour, and then a mixture of 0.1 g Pt(acac)\textsubscript{2}, 0.12 ml oleyamine, and 0.2 g 1,2-hexadecanediol was added to the solution; then the solution was heated up to reflux at 259 °C for 1 h. Small 4 nm FePt nanoparticles formed in this process are shown in Fig. 1(d). The idea here is to first produce Fe nanoparticles, which serve as nuclei, and then add Pt atoms to provide the monomers for further particle growth. The crystal structure of these particles is studied with XRD. The as-synthesized FePt particles have chemically disordered fcc crystal structure. Subsequent annealing of these nanoparticles deposited on silicon substrate is performed under a flow of Ar+5% H\textsubscript{2} at 500 °C, 600 °C, 650 °C, and 700 °C for 1 h. The structure transformation is seen in Fig. 4(b). With annealing, the peaks become narrower and shift to slightly higher angle, indicating both grain growth and ordering of Fe and Pt atoms. When annealed at 650 °C, two more peaks are clearly seen, which can be indexed as fct FePt structure, (001) and (002) plane, and confirm the formation of the ordered L\textsubscript{10} structure. At 700 °C, these two peaks are even more evident.

The as-prepared fcc FePt particles are superparamagnetic at room temperature as seen from the ZFC-FC magnetization measurements in the field of 10 Oe [Fig. 4(a)]. The room temperature hysteresis show that transformation of the structure with annealing temperature above 500 °C leads to a ferromagnetic behavior at room temperature. Coercive field after annealing at 650 °C is dramatically increased [Fig. 4(c)], and saturates after annealing at 700 °C.

**FIG. 4.** (a) ZFC-FC magnetic measurement of 4 nm FePt nanoparticles. (b) XRD patterns of FePt nanoparticles annealed at different temperature. (c) Room temperature hysteresis loops (in plane) of FePt nanoparticles deposited on silicon substrate at 400 °C and 700 °C, the inset shows the coercivity increases with annealing temperature, which becomes saturated after 700 °C.

**IV. CONCLUSION**

In summary, a general strategy of fabrication and characterization of magnetic nanoparticles with different morphologies and compositions is presented. By separating the nucleation and growth stage, different binary nanoparticles can be achieved, such as hard magnetic FePt nanoparticles and biocompatible air-stable Co–Au core-shell nanoparticles.

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