SYNTHESIS OF COLLOIDAL COBALT NANOPARTICLES WITH CONTROLLED SIZE AND SHAPES

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Abstract.- A method of producing high quality magnetic colloidal dispersions by the rapid pyrolysis of cobalt carbonyl in an inert atmosphere was employed to produce monodispersed, stabilized, defect-free ε-cobalt nanocrystals with spherical shapes and sizes ranging from 3 to 17 nm, as well as cubic and rod-like shaped particles. The size distribution and the shape of the nanocrystals were controlled by varying the surfactant composition (oleic acid, phosphonic oxides and acids), its concentration and the reaction temperature. These particles have been observed to produce 2D self-assemblies when evaporated at low rates in a controlled atmosphere. A combination of x-ray powder diffraction, transmission electron microscopy and SQUID magnetometry has been used to characterize both the dispersed nanocrystals and the assembled superlattices.

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Synthesis of metallic nanoparticles by wet chemistry routes is a powerful way to obtain reproducible macroscopic amount of homogeneous samples. Besides, with the growing interest in building advanced materials using nanoscale building blocks[1], there is a significant need for general approaches to control the size and shape of inorganic nanocrystals. This control obtained in some colloidal systems is by far one of the most versatile, reproducible and non-expensive procedure compared to other chemical or physico-chemical methods as electrochemistry, sonication, arc discharge, chemical vapor deposition, ion or electron beam patterning, etc.

The basic idea is to produce atoms in solution, which will immediately collapse into nanoparticles, and to control their final size and shape by means of a surfactant, or molecule, which will strongly absorb, selectively or not, to the nanocrystal surfaces. The surfactant has a role as controller of the crystal growth (by slowing it down or stopping it), the crystal shape (by attaching selectively to different crystal surfaces during growth) and the monomer concentration (by capturing atoms and releasing them later). In addition, the surfactant avoids particles agglomeration, makes the particles stable in solution and passivates them against oxidation.

Regardless of the way of producing atoms in solution, similar mechanisms in the nucleation and growing processes controlled by the surfactant are observed. Thus, different approaches like thermal decomposition, chemical reduction, UV reduction or Hydrogen reduction produces similar results as the nucleation and growing processes can be controlled[2]. In such ways, highly quality Au[3], Pt[4], Pd[5], Fe[6], Ni[7], Co[8], Ag[9] and its alloys like CoPt[10], FePt[11], PdPt[12], AuPd[12], AuAg[12]. In addition, similar results have been obtained in Co and Fe oxides[13] and semiconductors like CdSe[14].

Co nanocrystals display a wealth of size-dependent structural, magnetic, electronic, and catalytic properties. In particular, the exponential dependence of the magnetization relaxation time on volume has spurred intensive studies of Co nanocrystal synthesis for magnetic storage purposes. It is difficult to make isolated magnetic nanocrystals of Co, in part because the forces between the particles are large. These forces occur both due to the high electron affinity and high surface tension arising from the partially filled d-band, from the large van der Waals forces between polarizable metal particles, and finally from significant magnetic dipole interactions. Nonetheless, there has been considerable progress. Thus, Co[15,16] have recently been synthesized by solution phase metal salt reduction. Those particles generally display a multiple twinned crystal structure and chemical contamination from the reducing agent. Metal carbonyl pyrolysis have been largely used for many years to produce Co[17,18], Fe[19,6], Ni[7], CoPt[10] and other magnetic particles, but with a relatively large size distribution. Costly size selective precipitation methods are commonly required in order to obtain narrow enough size dispersion. This prior work suggests that Co is an excellent model system for nanocrystal growth kinetics studies.

In this paper we report the synthesis of nanoscale magnetic particles with spherical, cubic and rod-like shapes and their dispersion by self assembly into two dimensional arrays.

The nanocrystals are produced by the injection of an organometallic precursor into a hot surfactant mixture under inert (Ar) atmosphere. Tight size distributions can be obtained spontaneously when monomers can exchange between the particles, under conditions of "size distribution focusing"[20] before ripening[21] occurs. It is worth noting that Co is a challenging system because of its rich crystal phase diagram, with three nearly isoenergetic crystal structures (face-centered cubic, hexagonally close packed and epsilon).

A concentrated solution of $Co_2(CO)_8$ (0.40 to 0.80 g in 2-3 ml of o-dichlorobenzene anhydrous) was injected in an o-dichlorobenzene anhydrous refluxing bath (12 ml, T=181° C). The decomposition and nucleation occurs instantaneously upon injection. The lifetime of atoms in solution is short leading to the simultaneous formation of many small metal clusters (nuclei). The surfactant is present in the hot bath at concentrations of about 1% when the intermolecular distance is about few tenths of nanometer. Mixtures of oleic acid, trioctylphosphine oxide (TOPO) and hexil phosphonic acid (HPA) have been used. Control of the bath temperature and the surfactant composition modifies the strength of the metallic particle-organic molecule bonding. Thus, by controlling the precursor to surfactant ratio, the reaction temperature and injection time, the size of the spherical particles can be controlled and varied between 3 to 17 nm. This method may produce macroscopic quantities of Co single crystals that are monodisperse within the limit of atomic roughness (Fig.1b)[22].

There are only two stable crystal phases expected for elemental Cobalt at ambient pressures (hcp below 425°C and fcc at higher temperatures). However, in these samples, the Co particles display a complex cubic primitive structure (P_{4332}), related to the beta phase of manganese with 20 atoms present in a cube of 6.09 Å side (6.20 Å in the β-Mn), as described by Dinega et al.[18], and called ε-Co. In Fig.1a, an x-ray diffraction pattern for a sample of 10 nm spherical particles is shown. The broadening of the peaks (FWHM) indicates an average crystal size of 91 Å, which roughly corresponds to the particle size observed in transmission electron microscopy (TEM). X-ray emission spectroscopy and electron energy-loss spectroscopy (EELS) using nanometer-scale electron probes in a transmission electron microscope (TEM) confirmed that the particles are pure Co. High resolution phase contrast imaging (HREM) also showed that the particles are defect-free single crystals. In figure 2c, it is shown the diffraction patterns of a single ε-Co nanocrystal using a focused electron probe that confirms the Co cubic structure.

It has been recently shown that nanocrystals can self assembly in 2D and 3D arrays with long range translational and even orientational order[23]. Nanocrystals organize into close packed arrays simply by evaporating the solvent from a stabilized dispersion, provided that the size distribution of the particles is sufficiently narrow (i.e., a standard deviation about the mean diameter of less than 10%). Thus, these arrays may reproduce the nanoscale properties in macroscopic materials through homogeneity and periodicity and elicit collective electronic, magnetic and optical behavior resulting from the relative positioning of the nanocrystals in the array.

As already mentioned, in spite of the cubic crystal structure the particles grow with a spherical shape to minimize surface tension. Thus, by lowering the surface tension of the growing crystal, it may grow in a cubic shape. This phenomenon as also been observed in other materials as in Pt[4] or Au[24]. This is the case of the cubic crystals shown in Fig.2a. These crystals have been obtained with the same components mixture as the crystals obtained in Fig.1a (see Ref. 22), but lowering the temperature to 100 °C.

Second, anisotropic particles, nanorods, are obtained by rapid growth in a surfactant mixture (kinetic conditions)[25], where the different surfactants are used to control the growth rates of different faces selectively[26]. This is related with the selective catalytic power of the different crystal surfaces of Co, which indicates that different molecules attach with different strengths to different crystal faces, in such a way that some of them are more protected than others and the crystal is allowed to grow in a rod shape (Fig.2b). These rods spontaneously transform to more thermodynamically stable spheres of ε-Co if they are heated for a sufficient period of time. In Fig.2c, we see short fatty rods and with longer times (10 to 20 minutes), only spheres are observed.

As proof of the metallic and magnetic character of those crystals, measurements have been carried out to probe its magnetic properties. The samples where precipitated by adding anhydrous Methanol to the final solution and then centrifuged. The resulting powder was collected and introduced into a SQUID magnetometer. Some of this results are shown in Fig.3. Where it can be observed the rapid saturation of the magnetization and its low coercivity at 5 K and 300 K, indicating its metallic character, its soft magnetic behavior, and therefore the absence of Cobalt oxide, the crystal quality and suggesting a smooth surface of the particles.

A more detailed description of the synthesis and magnetic properties of Co particles maybe found in ref. 27.

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FIGURE CAPTIONS

Fig.1. a) XRD pattern ($\theta-2\theta$ *scan) of Co nanocrystal particles. All the peaks observed can be indexed as* ε*-Co. The peak widths confirm an average particle size of 9.1 nm. b) TEM image of a self-assembled 2D superlattice of 9 nm Co nanoparticles. c) Electron diffraction patterns using a focused probe of 8 nm diameter from a single* ε*-Co nanocrystal along the (210) and (001) zone axis. Bar 100 nm.*

Fig.2. TEM images of a) 25 nm Co cubes, b) 4:4:25 nm Co rods and c) 5:5:15 nm Co rods, respectively. Bar 100 nm.

Fig.3. Hhysteresis loops at 5 K and 300 K of 9 nm Co spherical particles.