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PREPARATION OF SELF-ASSEMBLED COBALT NANOCRYSTAL ARRAYS

J.S. Yin and Z.L. Wang
School of Materials Science and Engineering, Georgia Institute of Technology,
Atlanta, GA 30332-0245

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Abstract—Processing of self-assembled magnetic nanocrystals has vitally scientific and technological interests. In this paper, three different kinds of self-assemblies of cobalt nanocrystals were processed using particles processed by thermal decomposition of cobalt carbonyl in toluene. In case 1, two-dimensional self-assembly of cobalt nanocrystals with an average particle size of 9.2 nm and polydispersity of 9% has been formed. In case 2, macroscopic whisker structures composed of self assembled cobalt nanocrystals (with an average size of 8 nm) were formed during the thermal decomposition under an externally applied magnetic field. The whiskers can be aligned in the longitudinal axis direction during drying using an external magnetic field. In case 3, one-dimensionally ordered, densely packed self-assemblies have also been prepared using cobalt nanocrystals with irregular shape and larger particle sizes (10–20 nm). The formation of these different structures is attributed to the magnetic properties of cobalt particles with different sizes. *©1999 Acta Metallurgica Inc.*

Introduction

Naturally monodispersive nanocrystals and their physical and chemical functional specificity and selectivity suggest that they can be used as ideal building blocks for two- and three-dimensional cluster self-assembled superlattice structures (1–7). By adjusting the size of nanocrystals and the passivation molecular linkage between them, the properties of self-assembled artificial molecules are tunable. Up to date, ordered self-assembly of nanocrystals has been successfully fabricated for several materials, such as Ag (8,9), Au (10,11), α-Fe_2O_3 (12), CoO (13–15), CdSe (16), etc. But, to our knowledge, two-dimensional ordered self-assembly of magnetic materials is rather difficult because of the extra magnetic interaction among particles. Ordered two-dimensional magnetic nanocrystal arrays formed by self-assembly are of vital interests both scientifically and technologically because of their potential applications in high-density information storage. In ultrahigh density compact information storage media, the size of the domain determines the limit of storage density, while the sharpness of the domain boundaries is closely related to the media noise. If an ordered monolayer is formed by magnetic nanocrystals with sizes in a range of 10 to 20 nm, the density can be more than 1000 gigabits/in^2, which is a suitable material for storage density up to 1 terabits per square inch predicted for the 21st century (17). The noise reduction can be achieved by separating the magnetic nanocrystals by organic molecules adsorbed on the surfaces of the particles, thus, the media are composed of at least two materials: the magnetic clusters and the organic surfactant. The self-assembly passivated nanocrystal arrays are a potential candidate for solving this problem, in which the passivated surfactant serves not only as an isolation layer but also as a protection layer for the nano-magnets.

Recent self-assembly of cobalt nanocrystals (18) and nickel nanocrystals with sizes from 2 to 11 nm (19) has been reported, suggesting that ordered self-assembly of larger size magnetic nanocrystals is possible. In reference to the well-established magnetization studies of magnetic cobalt nanocrystals of others (20,24), cobalt nanocrystals larger than ~ 10 nm are particularly interesting for magnetic data storage because of the possibility of preserving ferromagnetic property. In this paper, we report the success of processing one-dimensional and two-dimensional self-assembled arrays of large size cobalt nanocrystals that may be adequate for high-density data storage. Whisker shaped self-assembly was also formed during synthesis by applying an external magnetic field. These different kinds of self-assembly configurations are the results of magnetic properties of the cobalt nanocrystals of different sizes, the surface adsorbed molecules, the externally applied magnetic field, and the drying method used.

Experimental

Cobalt nanocrystals were processed by thermal decomposition of $Co_2(CO)_8$ in toluene (20,25). $Co_2(CO)_8$, stabilized with 1–5% hexane, was commercially attained from Strem Chemicals Inc. Toluene was from Fisher Chemicals with a purity of 99.8%. The decompositon was carried out under argon to minimize oxidation. Homogenous nucleation and growth were maintained to grow monodispersive nanocrystals. To avoid agglomeration of the freshly nucleated nanocrystals, sodium bis(2-ethylhexyl) sulfosuccinate (in short, Na(AOT), from Aldrich Chemicals) was added as a surface active agent at the beginning of the growth, forming a monop-layer passivation over the nanocrystal surface. The sulfate serves not only as the protection layer for the particles to avoid direct contact between the particles, but also the inter-particle bonding. Typically, 100 mg of $Co_2(CO)_8$ and 20 mg of Na(AOT) were dispersed into 25 ml of toluene at room temperature, then the mixed solution was ultrasonically dispersed externally and heated at 120°C for 5 hours. Following the systematic study of Papiper et al (26), the average size of nanocrystals was optimized by controlling the temperature and concentration. Then the mixed solution was diluted by adding three volume parts of toluene into one part of the solution. The as-prepared solution may contain some impurities and oxides. A size and phase selection was required to obtain Co nanocrystals with specific size and even shape. Since cobalt oxides (CoO and Co_3O_4) are anti-ferromagnetic, a small magnetic field, generated by a horseshoe permanent magnet, was applied in the vertical direction to make the phase selection of Co from its oxides. The cobalt nanoparticles floated to the top surface of the liquid under the driving force of the magnetic field, while the oxide particles were left in the solution. Though there was gravity force, the smaller size particles could still suspend in the liquid because of the Brownian motion, while the larger ones sank to the bottom. By selecting the particles suspended at the surface of the solution after 24 hr in the magnetic field, the pure cobalt nanoparticles were obtained. To improve the crystallinity, the diluted solution was heated in an enclosed flask for 48 hours at 100°C. Finally, the large size agglomerations were removed from the solution by centrifugal at 1000 rpm for 2 minutes, and the remaining dispersive nanocrystals were used for self-assembly. More detailed experimental procedures will be given describing the three cases.

The structure of the nanocrystals was determined at 200 kV using a Hitachi HF-2000 transmission electron microscope (TEM) equipped with a field emission source. A droplet of the solution was deposited on an ultra-thin carbon film and the support was holding vertically so that the gravity may drive the motions of the nanocrystals suspended in the solution. We found this is an effective way in forming ordered self-assembly. The droplet was left in air and it usually takes ~ 2 min. to dry.

Results and Discussion

Two-Dimensional Assembly of Superparamagnetic Cobalt Nanocrystals

Figure 1 shows a TEM image of a monolayer assembly of cobalt particles whose sizes are in the range of 4–9 nm. The self-assembly is formed by differentiating in sizes, forming a monolayer structure with

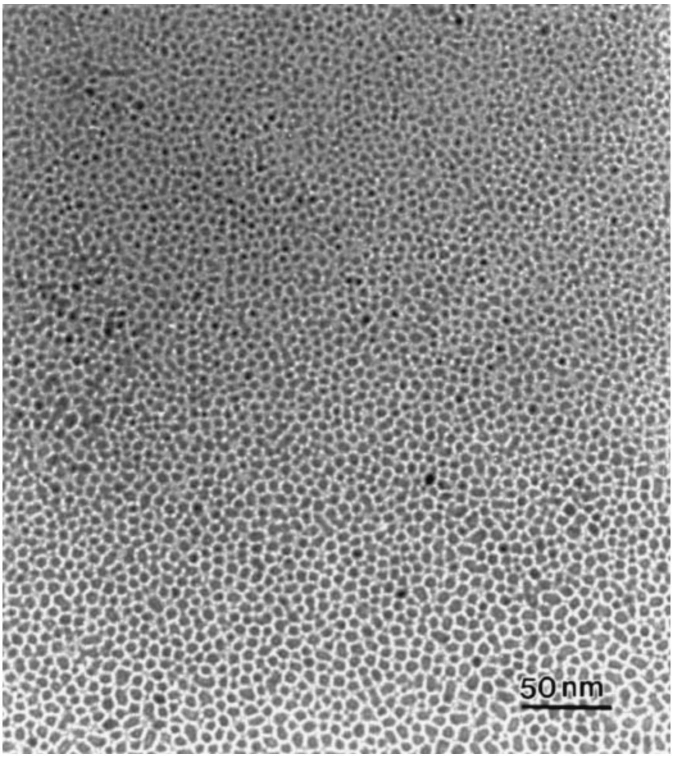

Figure 1. Self-assembly of the size unselected cobalt nanocrystals (4–9 nm), showing size differentiation in the perpendicular drying process.

close packing. These particles are likely to be superparamagnetic, thus, the inter-particle magnetic interaction is negligible. The gravitation force and the surfactant molecules can take a significant role in selecting the size and forming the packing. In the vertical drying technique, the gravity force might help to organize the particles with different sizes even the drying time of the liquid was short.

Figure 2 shows a TEM image recorded from a 2D self-assembly of cobalt nanocrystals with an average particle size of $\sim$ 9.2 nm and polydispersity 9%. This is the size range in which the ferromagnetism transforms into superparamagnetism. The cobalt particles are crystalline and are dominated by the face-centered cubic structure, as proved by the electron diffraction pattern shown in the inset. Typically, the intensity of {111} ring is stronger than that of {200}. This also serves as a criterion to rule out the possibility of cobalt monoxide because the intensity of the {111} ring for cobalt monoxide is weaker than that of its {200}. This result was also confirmed by chemical microanalysis using energy dispersive x-ray spectroscopy (EDS). The inter-particle surface-to-surface distance is $\sim$ 2 nm. The relatively narrow size distribution is important for forming the ordered assembly.

Aligned Self-Assembly of Cobalt Nanocrystals under an External Magnetic Field

The assembly of magnetic nanocrystals is strongly influence by an externally applied magnetic field. To demonstrate this effect, an alternating magnetic field (26) was applied to the liquid during the synthesis. A droplet of the solution was deposited on a clean glass plate for microscopy examination. Figure 3a is an optical micrograph of the as-synthesized whiskers of cobalt nanocrystals, showing whisker-shaped assembly with random orientations. The typical length of the whiskers is $\sim$ 50–80 μm

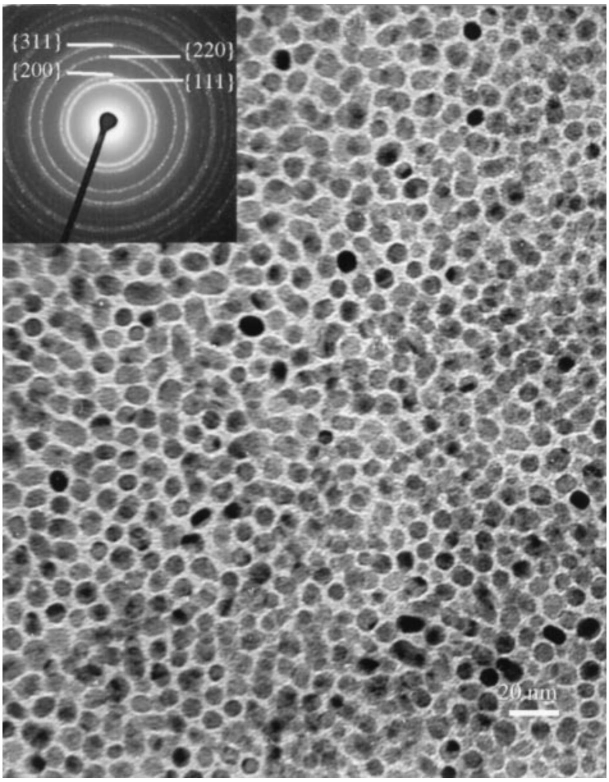

Figure 2. Ordered self-assembly of cobalt nanocrystals. The inset is an electron diffraction pattern (SAD) from the nanocrystals showing the face-centered cubic structure.

and the width of $\sim 5\ \mu$m. The whiskers can be taken as a nano-composite of cobalt nanocrystals with the Na(AOT) organic molecules. It must be pointed out that this whisker structure was not formed in the self-assembly of cobalt nanocrystals at the absence of the magnetic field, rather some irregularly shaped nanocrystal agglomerations as well as dispersed cobalt nanocrystals were observed.

Figure 4a is a low magnification TEM micrograph recorded from the whiskers, exhibiting uneven shapes of the assembly. Figure 4b is a magnified image from a thin part of the whisker, showing a uniform distribution of cobalt nanoparticles in the composite. The sizes of the nanocrystals are measured from the TEM images and are in the range of 5–8 nm. To determine the crystal structure of the cobalt particles, selected area electron diffraction patterns are recorded (Figure 4c). The three main rings are indexed as the {111}, {200} and {220} rings of a face-centered cubic system, indicating the *fcc* structure of cobalt particles, which is in agreement with that of others (20).

To determine the possible magnetization preserved in the whiskers, a droplet of the as-prepared solution containing the whiskers was deposited on a glass plate when an external magnetic field was applied parallel to the glass plate. The specimen was then examined by optical microscopy after a slow drying (Figure 3b). It is very clear that most of the whiskers are aligned along the field direction, unambiguously indicating the ferromagnetism of the nanocomposite although each particle is believed to be superparamagnetic. This experiment suggests that a self-assembly of cobalt nanoparticles, under an external magnetic field, results in a transition from superparamagnetic cobalt particles to a ferromagnetic whisker structure.

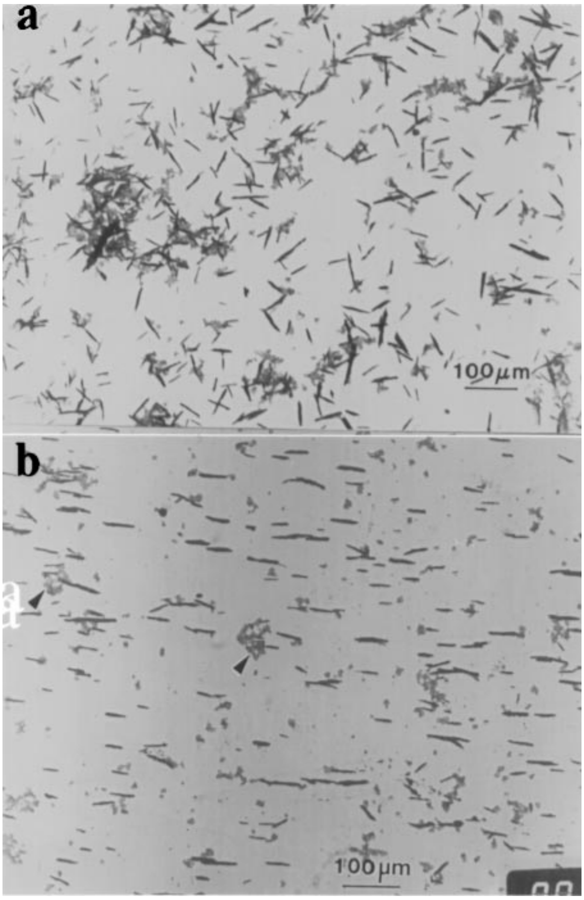

Figure 3. (a) Optical micrograph of the as-prepared cobalt nanoparticle composites, showing the formation of anisotropy whiskers in the solution and the random orientation of the whiskers. (b) Optical micrograph of the whiskers deposited on a glass plate with the presence of a magnetic field during the drying process, showing the alignment of the whiskers along the field direction.

Ordered Self-Assembly of Ferromagnetic Cobalt Nanocrystals

For particles with larger size, the magnetic interaction among the particles may influence the assembly structure. For cobalt nanocrystals with sizes of 10–20 nm, the dipole-dipole interaction among the magnetic particles may become stronger than that of thermal vibration energy so that the nanocrystals can form oriented chains. In the colloidal solution with nanocrystals, the mobility of nanocrystals in the liquid allows them to find the lower energy positions during the drying process. Figure 5a is an array formed by the aligned cobalt nanocrystals. The highly ordered assembly of the particles along a particular direction is likely to be associated with the magnetic moment alignment among the particles. This type of magnetic interaction induced assembly is supported by the theoretical calculation (21). A closer examination of the particles shows that the particles may have non-spherical shape, with their longer axis parallel to the alignment direction (Figure 5b). This result strongly suggests that the anisotropy structure of the particles may be the origin of magnetic alignment and the longitude direction is the aligned domain direction.

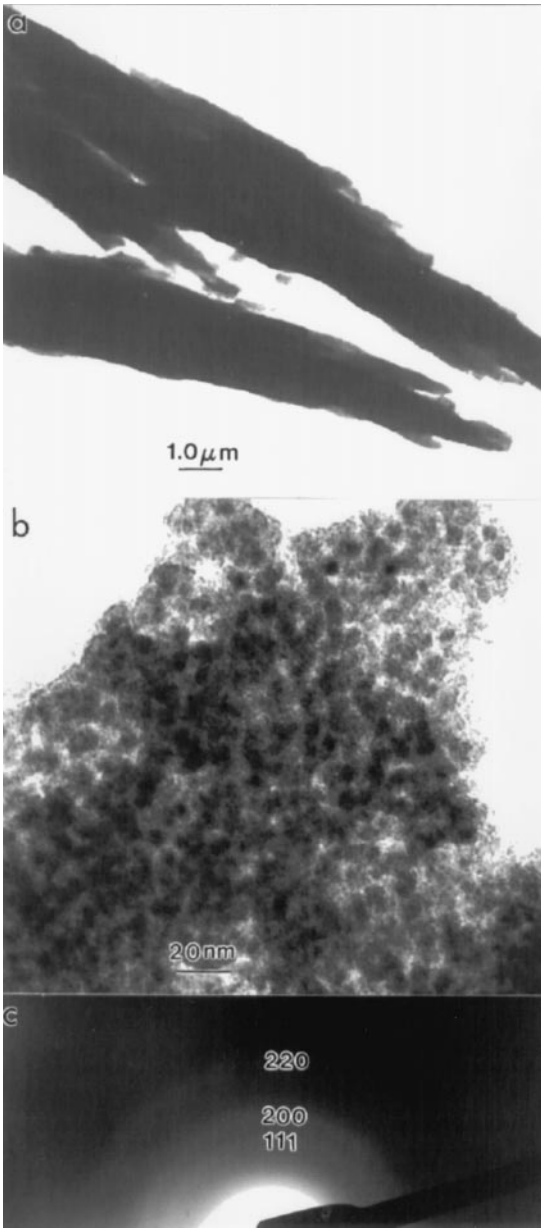

Figure 4. (a) A low magnification TEM image of the whiskers, (b) an enlarged TEM image of a whisker showing the cobalt nanoparticles with sizes of 5–8 nm, and (c) an electron diffraction pattern recorded from cobalt particles illustrating the face-centered cubic structure of the particles. The diffraction pattern is diffuse because of the presence of polymer and the low processing temperature.

The newly observed aligned structure of nanoparticle assembly is much different from that of chain-like zig-zag packing of large cobalt particles (20,22) possibly because the large particles may be composed of multi-magnetic domains. The structure shown here is also different from that of thin cobalt films produced by sputtering techniques, which shows no preference of orientation (23). Magnetic

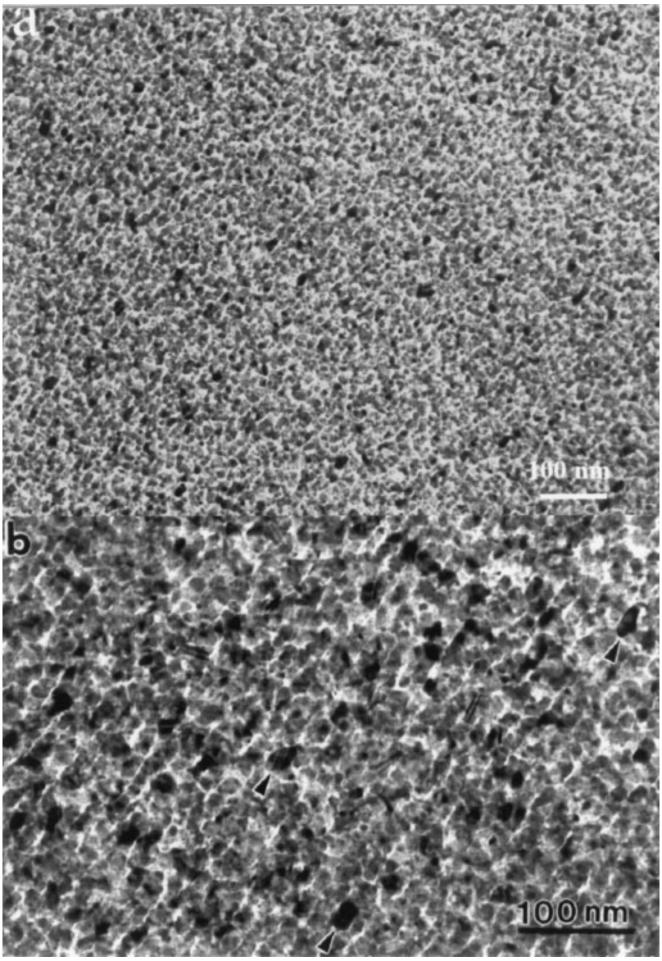

Figure 5. One dimensional self-assembly of cobalt nanocrystal arrays with sizes of 10–20 nm. (a) A low magnification view and (b) a higher magnification view showing the anisotropy shapes of the ferromagnetic nanocrystals. The arrowheads indicate the alignment of the longitudinal directions of the particles with the assembling direction.

properties, such as enhanced coercive force and remanence-to-saturation ratio, can be enhanced by the ordering of magnetic nanocrystals. This effect can be explained by the dipole coupling between the nanocrystals and the increased energy barrier for magnetization reversal of the ordered structure (20).

Conclusions

Ordered self-assembly of cobalt nanocrystals has been prepared by a simple technique. In case 1, two-dimensional self-assembly of cobalt nanocrystals with an average particle size of 9.2 nm and polydispersity of 9% has been formed by a gravitation differential fast-drying method. In case 2, the whisker shaped assembly of cobalt nanocrystals (5–8 nm) can be formed during the thermal decomposition under an applied magnetic field, which tends to align the magnetic momentum of the Co nanocrystals. The whiskers can be aligned macroscopically during drying on a glass substrate by an external magnetic field. It is proved that a self-assembly of cobalt nanoparticles, under an external magnetic field, results in a transition from superparamagnetic cobalt particles to a ferromagnetic whisker structure. In case 3, one-dimensionally ordered, densely packed self-assembly of cobalt nanocrystals with irregular shape and larger particle sizes (10–20 nm) is a unique structure that may have potential application in ultrahigh density data storage.

Acknowledgments

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