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Self-assembly of FePt nanoparticles into nanorings

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The application of nanoparticles as quantum dots in nanoelectronics demands their arrangement in ordered arrays. Shape controlled self-assembly is a challenge due to the difficulties of obtaining proper self-assembling parameters, such as solvent concentration, organic ligands, and nanoparticle size. In this article, hard magnetic FePt nanoparticles were synthesized using a combination approach of reduction and thermal decomposition. The nanoparticles are about 4.5 nm and appeared as truncated octahedral enclosed by the {100} and {111} crystal facets of fcc structure. The nanoparticles are of hexagonal close packing and orient randomly in the self-assembly nanoarrays. By diluting the solution for large-area self-assembly, monolayer, submonolayer, and multilayer nanorings of FePt nanoparticles were formed. The nanoring formation is determined by hydrodynamics, surface effects, and interaction between the FePt nanoparticles and substrates.
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Nanoparticles show many unique optical, electric, magnetic, and catalytic properties that are greatly different from both the corresponding bulk materials and the individual atoms of which they are composed.^{1–6} The application of these nanoparticles as quantum dots in nanoelectronics demands their regular arrangement in ordered one- (1D), two- (2D), and three-dimensional (3D) arrays.⁷ Various kinds of 1D, 2D, and 3D ordered arrays have been achieved by the self-assembling method.^{4–11} The self-assembling arrays can be tuned by nanoparticle size, organic ligand, solvent concentration, etc. It is essential to manipulate the nanoarrays to various kinds of shapes and patterns for the nanoelectronics applications.¹²

Fe–Pt alloys have been studied for decades because of their important applications in permanent magnetism.^{13–17} Self-assembling FePt nanoparticles have attracted more researchers due to their excellent hard magnetic properties and potential application on ultrahigh density magnetic recording media.^{18–20} In this article, we report direct self-assembly of FePt nanoparticles into monolayer, submonolayer, and multilayer nanorings.

The FePt nanocrystallites were prepared by following Sun's method using a combination approach of reduction and thermal decomposition in the presence of oleic acid and oleyl amine.^{17–20} A slightly modified synthetic procedure is as follows: Under airless conditions, platinum acetylacetonate (Alfa, 99 mg, 0.25 mmol), 1,2-tetradecanediol [Aldrich; 192 mg (purity: 90%), 0.75 mmol] and dioctylether (20 ml) were mixed and heated to 100 °C. Oleic acid [Aldrich, 0.09 ml (purity: 90%), 0.25 mmol], oleyl amine [Aldrich, 0.12 ml (purity: 70%), 0.25 mmol], and Fe(CO)₅ (Aldrich, 0.065 ml, 0.50 mmol) were added successively. The mixture was refluxed at 297 °C for 30 min and then naturally cooled down to room temperature under the flow of argon gas. At this

moment, nanocrystalline FePt was formed as a seed. Subsequently, similar amounts of platinum acetylacetonate, 1,2-tetradecanediol, oleic acid, oleyl amine, and Fe(CO)₅ were added into the flask using the same procedure when the system was heated up again. After the refluxing continued for additional 30 min, the mixture cooled down to room temperature under an argon atmosphere. The nanoparticles were first precipitated by adding a combination of polar solvents (7.5 ml of hexyl alcohol + 20.0 ml of ethanol) and followed by centrifugation. The precipitate (FePt) can be redispersed into hexane followed by a size-selection treatment. The selected FePt nanoparticles were eventually redispersed in a mixed solvent of (95% octane + 5% octanol). The suspension was then diluted by using octane, followed by one drop on a transmission electron microscopy (TEM) grid and evaporated in a vacuum for self-assembling nanorings.

Monodisperse FePt nanoparticles arrays can be obtained after the size selection. Figure 1(a) shows (111) ordered arrays, in which the nanoparticles have hexagonal close packing. The as-synthesized FePt nanocrystals have a chemically disordered face-centered cubic (fcc) A1 phase.^{21,22} The crystal structure can be determined by selected-area diffraction pattern (SAD) as shown in Fig. 1(b). The ratio of Fe and Pt concentration is close to 1:1 by EDS analysis. The nanocrystals appeared as polyhedral shapes. The truncated octahedral nanoparticles were dominated in the synthesis as shown in the insert in Fig. 1(a). The truncated octahedral is enclosed by the {100} and {111} crystal facets of the fcc structure. The size of the nanoparticles is about 4.5 nm. The orientations of nanocrystals in the self-assembling nanoarrays are quite random, which is different from the Ag self-assembling arrays reported by Harfenist *et al.*,⁵ in which the Ag nanoparticles oriented to the same orientation with the nanocrystal lattice. The orientations of the nanoarrays in our samples seem to have less relationships with those of single nanocrystals.

The nanorings were obtained by simply diluting the suspension for large-area self-assembling and dropping it on

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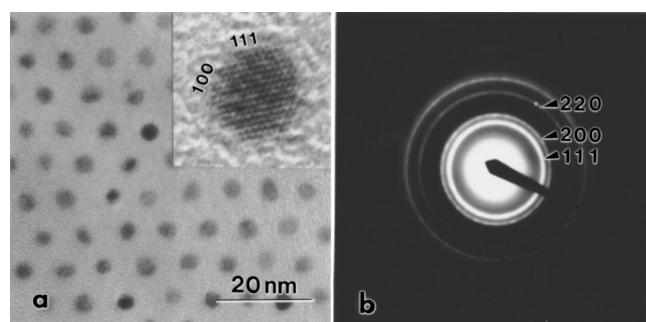


FIG. 1. (a) Monodisperse FePt nanocrystal self-assembly arrays. (b) SAD pattern of FePt nanoparticles. The insert is a high-resolution TEM image of FePt truncated octahedral nanoparticle.

TEM grids. Figure 2(a) is a monolayer nanoring of FePt nanoparticles. The nanoparticles inside the ring also formed ordered arrays. The diameter of the nanoring is about 550 nm and the thickness of the wall is about 30 nm. The diameter and wall thickness of the nanorings vary from each other. Few nanoparticles can be seen both inside the ring and the outside. The submonolayer rings were often observed. The diameters of the nanoring in Fig. 2(b) is 420 nm and the thickness of the wall is about 100 nm. The FePt nanoparticles in the second layer occupied the two-fold saddle and three-fold hollow sites of the first layer arrays and formed superlattice and ring packing toward the inner rim of the nanoring.²³

Multilayer nanorings were first observed as shown in Fig. 3(a), in which the diameter of the nanoring is 800 nm and thickness of the wall is more than 400 nm. The first three layers can be clearly identified as denoted by arrows 1, 2, and 3 in Fig. 3(a). The nanoring becomes darker toward the inner rim, which implies multilayer packing was formed. It seems that upper layer nanoparticles were pushed out toward the rim and formed multilayer packing during self-assembly. Again, only a few extra nanoparticles were observed inside and outside the ring. In our experiment, the suspension concentration was the main parameter to control the formation of nanorings. It is hard to tell the exact concentration for forming the nanorings. However, the swamplike pattern would always be observed before further diluting the suspension and obtaining ring structure. Figure 3(b) is a swamplike self-assembling pattern of FePt nanoparticles. The size of the “swamps” varies from each other, but close to the ring diameter and the concentration for forming swamp pattern is close to the critical concentration for forming ring structure as well.

Ring formation is a complex process.^{24–26} It is determined by hydrodynamics, surface effects, interaction between self-assembling subunits, and substrates. When nanoparticle solutions were dropped on the carbon grid, the liquid thin film was believed to have formed.²⁴ As the liquid thin-film thickness reached a critical value, holes opened in order to restore the film to its equilibrium thickness. The holes nucleated and grew bigger due to evaporation-driven instability. The advance of the growing hole rims in the solvent film was stopped when the radial force outward was no longer sufficient to overcome the frictional effects of the

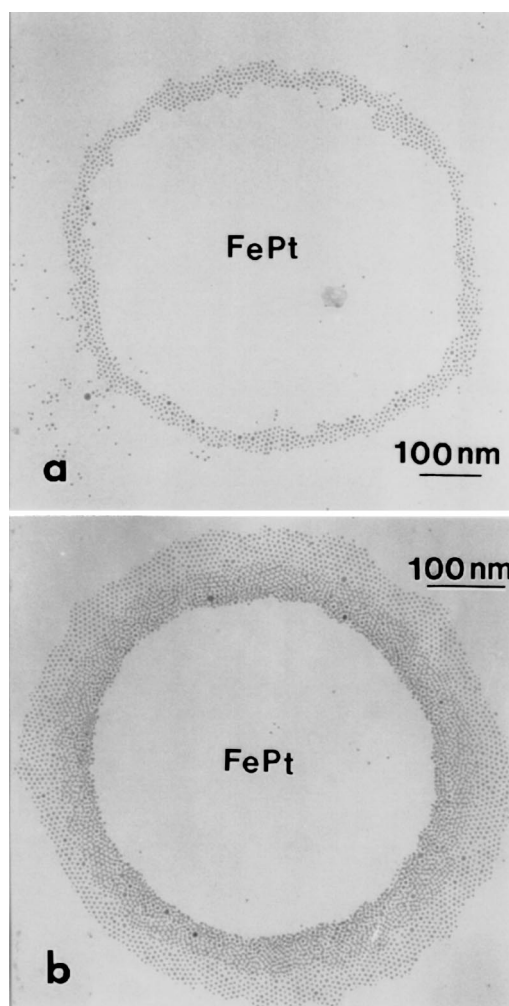


FIG. 2. (a) Monolayer FePt nanoparticle ring. (b) Submonolayer FePt nanoparticle ring.

nanoparticles which had been collected in the rim. The holes nucleated and pushed nanoparticles outward and left few nanoparticles inside and outside the rings, and friction effects of nanoparticles also kept the thickness of the upper layer wall of the nanoparticle ring thinner than the lower layer in multilayer ring formation. In our observation, different sizes and configurations of nanoring patterns were observed. The concentration of the suspension may have been very critical for forming nanoparticle rings in our system. The high concentration of the suspension generally induced the formation of large-area self-assembly or swamplike patterns. The proper concentration generated ring “seeds” for nanoparticle ring formation. The concentration of local ligands, evaporation rate of the solution, and the interaction between the nanoparticles and substrate control the configurations of the nanorings. The monolayer nanoring formation can be easily explained by the aforementioned theory. For the submonolayer and multilayer rings, the local concentration of the solution may have caused the nanoparticles to form 3D packing. As the liquid thin film reached a critical thickness, the holes were formed and the advance of the growing holes after the solvent evaporation pushed the multilayer arrays outward and formed multilayer packing. As the radial force

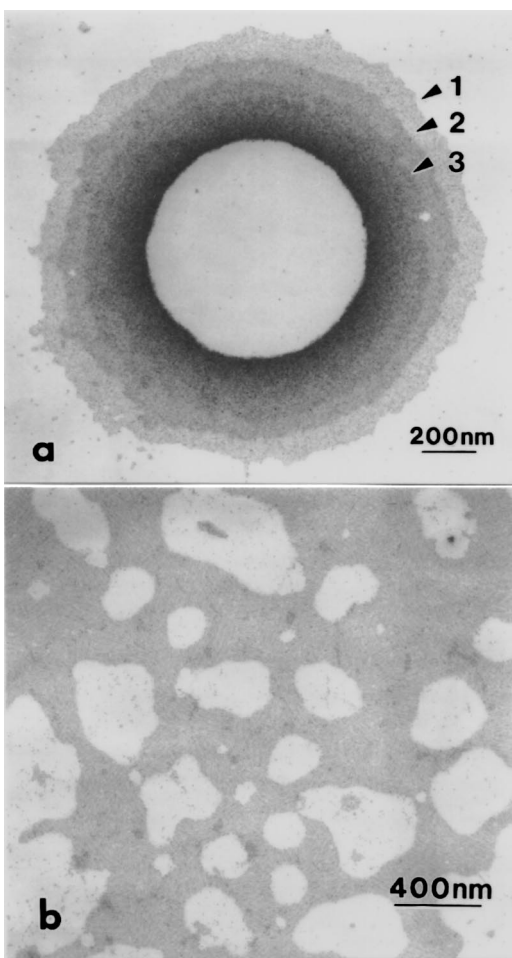


FIG. 3. (a) Multilayer FePt nanoparticle ring. (b) Swamplike pattern of FePt self-assembling arrays.

outward was no longer sufficient to overcome the frictional forces generated from the different layers of nanoparticles, the multilayer rings were formed as denoted by 1, 2, and 3 in Fig. 3(a). This was very hard to identify after accounting for the three layers since the darker contrast of the inner layer implies more layer packing of the nanorings was formed. It is not yet known how much the magnetic moments of the nanoparticles contribute to the ring formation during the self-assembling process. Closely checking for the monolayer nanoring indicated that the distance between two particles was too big for the magnetic dipolar interaction. However, there were magnetic dipolar interactions between the multilayer nanoring formations due to close contacts among nanoparticles of different layers. It is believed that dipolar interaction competes with nondirectional van der Waals interactions at close range and the ring formation is directed by the magnetic moments.²⁷ In our case, the multilayer rings are always concentric circles, which implies that magnetic dipolar interaction among the nanoparticles may stabilize the nanorings and make the energy and magnetic preference in the multilayer packing system, which is different from other nonmagnetic nanoparticles.²⁸

The subhundred nanometer spin-dependent electronic devices with nanometer-scale control of material properties in all dimensions have been studied by an IBM group.²⁹ The nanorings formed by FePt magnetic nanoparticles have a potential role in the magnetotransport in nanostructured materials. Size and configuration control of the nanorings are under tuning, which may provide collective magnetic configurations for the magnetic nanoparticle rings.³⁰

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