Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp455-456

Self-assembly Patterning of "Quasi-Superparamagnetic" Magnetite Nanooctahedra

Jun Min Xue

Department of Materials Science and Engineering,
National University of Singapore, Singapore, 117576
Phone: 65-65164655 E-mail: msexuejm@nus.edu.sg

1. Introduction

Regular pattern with nanometer-scaled feature size has been an important step towards rational design of novel devices in nanoelectronics, nanophotonics and/or nano-magnetics [1,2]. To make well patterned and stable nano-structures from nanoparticle building blocks, it is required that the nanoparticles have a well defined size and shape and that the interaction among these building blocks can be tuned to allow the system to reach a minimum free-energy state [3]. Besides the size and shape of the nanoparticles, the interaction force between the nanoparticles also has a profound influence on the nanoparticle organizations [4], and it becomes more important if the nanoparticles are assembled in a large area. Generally, there are two major interparticle forces existing in the nanoparticle systems. The first force is the van der Walls force, which induces the self-assembly, whereas the second is the repulsive force between nanoparticles that is mainly from their attachments. The stable self assembled structures are achieved as the result of the balancing of these two forces [5]. However, the attractive van der Walls force between nanoparticles is normally weak, which is easy to be disturbed by several uncertain factors, such as surface defects on substrates and defects in nanoparticles. This makes the self assembly of nanoparticles at a large area nearly impossible. In order to optimize the assembling of nanoparticles in a large area, it is necessary to introduce a more manageable interaction force between nanoparticles. The magnetic dipole-dipole interactions give another dimension in the self-assembly control.

In this work, a stable patterned structure of large size has been realized with magnetite nanooctahedra of 21 nm in diameter. The 21 nm magnetite nanooctahedra show relatively weak ferromagnetic characteristics at room temperature with a superparamagnetic blocking temperature close to room temperature. These "quasi-superparamagnetic" nanocrystals are easy to be magnetized and the magnetization and dipole-dipole interactions can be retained at the room temperature. A simple two-phase set up was developed to conduct the assembly of the nanooctahedra. By applying a relatively weak magnetic field (600 Oe or 0.06 T) in horizontal, a 2D monolayer patterned structure was formed. The resultant structure showed high degree of both translational and orientational order over a large area of 10 x 10 μm.

2. Results and discussion

The 21-nm magnetite nanooctahedra were synthesized through a thermal decomposition method. As shown in **Figure 1A**, the magnetite nanoparticles were randomly spread on the TEM copper grid. The random distribution of the nanoparticles was also reflected by the corresponding ring-like diffusion pattern of selected area electron diffraction (SAED) (Inset of **Figure 1A**). HRTEM image of an isolated nanoparticle was shown in **Figure 1B**, from which the lattice spacing was measured to be 0.295 nm, which matched well with the standard *d* spacing of magnetite (220) at 0.297 nm. **Figure 1C** shows a schematic representation of the truncated magnetite nanooctahedron. The length between the two opposite vertices was taken as the particle size. A close look at the TEM image (**Figure 1A**) revealed that two magnetite nanooctahedra were piled up together at most areas (the areas circled in red are more noticeable than others), forming a double layered assembling structure due to dipole-dipole interactions, as demonstrated in **Figure 1D**.

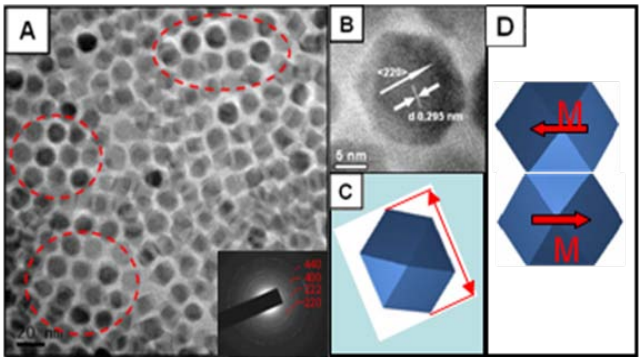

Figure 1: (A) TEM image showing the as-synthesized 21 magnetite nanooctahedra before applying any magnetic field (Inset: the corresponding selected area electron diffraction (SAED) pattern). (B) HRTEM image showing a single 21 nm nanooctahedra and its lattice spacing. (C) A schematic illustration of a truncated nanooctahedron. (D) A schematic illustration showing that two nanooctrahedra were piled up due to the dipole-dipole interaction.

The double layered structure can be dramatically changed into a highly ordered monolayer structure by applying a weak magnetic field. A simple set up, so-called two-phase set up, was designed to assemble the "quasi-suparaparamagnetic" nanooctahedra into ordered structure. The schematic illustration of the set up was shown in **Figure 2A**. **Figure 2B** presents the SEM image of the as-prepared ordered structure made of 21 nm-sized magne-

tite nanooctahedra on a silicon substrate. A uniform monolayer of nanoparticles was observed and the typical sample size was around 1cm x 2cm, as shown in **Figure 2C**. The ordered monolayer structure was also transferred onto TEM copper grid in a same way for TEM observation. As shown in **Figure 2D**, a defect free monolayer superlattice structure by nanoparticles was formed successfully onto the TEM grid. The higher magnification TEM image zooming in a smaller area revealed that the nanooctahedra were arranged in a hexagonal close packed manner (**Figure 2E**). **Figure 2F** demonstrated the Fast Fourier Transformation (FFT) image corresponding to **Figure 2E**. A nearly perfect three-fold symmetry was observed, which agreed with the hexagonal packing pattern. Moreover, the equivalent lattice spacing measured from FFT pattern was comparable with the actual particle size. The distinct texture of the magnetic field induced monolayer was easily grasped by evaluating the corresponding SAED pattern, as shown in **Figure 2H**. The superlattice presented a single crystal-like, or so called "supercrystal" [6] electron diffraction pattern, indicating that the obtained structure not only had the regular translational pattern but also crystallographic orientation. The "supercrystal" was indexed as [111] texture direction of spinel magnetite.

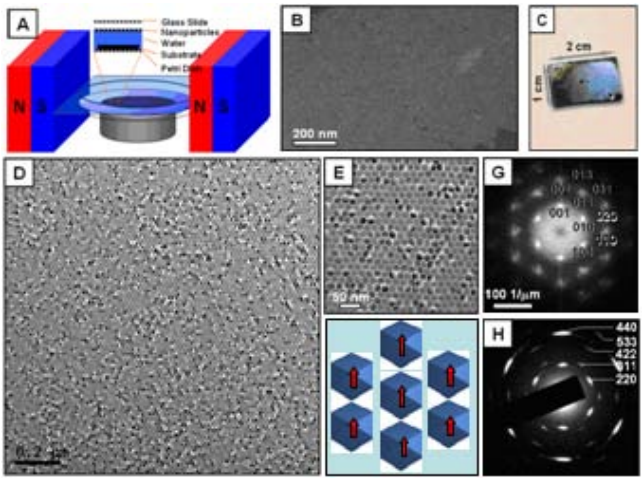

Figure 2: (A) A two-phase set up was designed to organize magnetic nanoparticles into patterned structure by applying an external field. (B) An SEM image showing the 2D patterned structure by magnetite nanooctahedra on a silicon substrate. (C) A digital picture showing the silicon substrate with size of 1 cm x 2 cm. (D) A TEM image showing the 2D "supercrystal" structure formed with magnetite nanooctahedra induced an external magnetic field of 600 Oe. (E) A high magnification TEM image showing the ordered arrangement of the nanoochedra in the "supercrystal" structure. (F) A Fast Fourier Transformation (FFT) image demonstrating the hexagonal close packing of the nanoochedra in the "supercrystal" structure. (G) A schematic illustration showing the hexagonal close packing of the nanooctahedra. (H) The SAED pattern of the superlattice structure formed by the nanooctahedra, confirming that all the nanooctahedra were aligned in crystallographic orientation.

The magnetic field plays an important role in organizing the nanooctahedra into the 2D "supercrystal" structure. Without the external magnetic field, the magnetite dipoles were in a random manner. In order to reach the minimum free energy state, every two nanoparticles were piled together, forming a disordered double layered structure. When a magnetic field was applied, the dipoles were aligned in the easy direction [111] of the nanooctahedra along the field. The head-to-tail arrangement of nanoparticles along [111] texture direction was then preferred and the dipolar forces between the nanooctahedra promoted the formation of the 2D "supercrystal". The strength of the dipolar forces is critical for the final appearance of the "supercrystal". As demonstrated in **Figure 2**, when the magnetic field was 600 Oe, the dipolar forces had a good balance with the intrinsic interactions between the nanoparticles including van der Walls force and repulsion from the surfactant attachements, inducing a perfect hexagonal close packed "supercrystal" structure (**Figure 2G**). The quasi-superparamagnetic behavior of the 21 nm nanooctahedra also plays a crucial role in the formation of the 2D supercrystal structures. It was observed that chain-like structures were formed by 53 nm magnetite octahedra which showed ferroelectric behavior at room temperature without applying any magnetic field. A relatively weak magnetic field (600 Oe) was not able to re-organize these chain-like structures due to the strong dipole interactions between the ferroelectric 53 nm nanocrystals.

3. Conclusions

In summary, we have reported that 2D superlattice structure could be formed with "quasi-superparamagnetic" nanooctahedra in the presence of a weak magnetic field of 600 Oe. The assembled structures were organized in a hexagonal close packing manner, which demonstrated both translational and crystallographic order at a large area of 10 x 10 μm. The strength of the magnetic field and the "quasi-superparamagnetic" behavior of the nanooctahedra were two crucial factors for the successful formation of the 2D superlattice. The strategy to use "quasi-superparamagentic" magnetite nanooctahedra to form a stable superlattice structure may be extended to other magnetic systems and find potential applications such as high density data storage.

Reference:

[1] Bita, I.; Yang, J.K.W.; Jung, Y.S.; Ross, C.A.; Thomas, E.L.; Berggren, K.K. Science, 2008, 321, 939.
[2] Ruiz, R.; Kang, H.; Detcheverry, F.A.; Dobisz, E.; Kercher, D.S.; Albrecht, T.R.; Pablo, J.J.de.; Nealey, P.F. Science, 2008, 321, 936.
[3] Puntes, V.F.; Krishnan, K.M., Alivisatos, A.P. Science, 2001, 291, 2115.
[4] Talapin, D.V.; Shevchenko, E.V.; Murray, C.B.; Titov, A.V.; Kral, P. Nano Letters, 2007, 7, 1213.
[5] Narayanan, S.; Wang, J.; Lin, X. M. Phys. Rev. Lett. 2004, 93, 135503.
[6] Bentzon, M. D.; Van, Wonterghem, J.; Moerup, S.; Tholen, A. Koch, C. J. W. Philos. Mag. B 1989, 60, 169.