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Nanostructures of gold coated iron core-shell nanoparticles and the nanobands assembled under magnetic field

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Abstract. Pure metal iron nanoparticles are unstable in the air. By a coating iron on nanoparticle surface with a stable noble metal, these air-stable nanoparticles are protected from the oxidation and retain most of the favorable magnetic properties, which possess the potential application in high density memory device by forming self-assembling nanoarrays. Gold-coated iron core-shell structure nanoparticles (Fe/Au) synthesized using reverse micelles were characterized by transmission electron microscopy (TEM). The average nanoparticle size of the core-shell structure is about 8 nm, with about 6 nm diameter core and 1∼2 nm shell. Since the gold shell is not epitaxial growth related to the iron core, the morié pattern can be seen from the overlapping of iron core and gold shell. However, the gold shell lattice can be seen by changing the defocus of TEM. An energy dispersive X-ray spectrum (EDS) also shows the nanoparticles are air-stable. The magnetic measurement of the nanoparticles also proved successful synthesis of gold coated iron core-shell structure. The nanoparticles were then assembled under 0.5 T magnetic field and formed parallel nanobands with about 10 μm long. Assembling two dimensional ordered nanoarrays are still under going.

PACS. 68.37.-d Microscopy of surfaces, interfaces, and thin films – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 75.75.+a Magnetic properties of nanostructures – 75.50.-y Studies of specific magnetic materials

1 Introduction

Currently, one of most versatile methods to synthesize core-shell structure is wet chemical method such as microemulsion techniques which relies on the self-assembly nature of surfactants to push aqueous reactants into micelle [1]. The idea is from successful improvement of the quality of the particles to achieve chemical passivation of the surface of the crystallites, which has been applied on inorganic coating of semiconductor nanoparticles [2–8]. Due to the dynamic nature of micelles, aqueous components can come together and react to form particles that are constrained to the size of the micelle. By changing the reaction conditions the methods can be even applied sequentially to form core-shell structure. By careful controlling of the synthesis using reserve micelles the nanoparticles can be obtained in a very narrow size distribution and quite uniform.

Pure metal iron nanoparticles are unstable in the air. By a coating an iron nanoparticles with a stable noble metal like gold, these air-stable nanoparticles are protected from the oxidation and retain most of the favorable magnetic properties, which possess the potential application in high density memory device by forming self-assembling nanoarrays. Recently spin-dependent tunneling was measured in self-assembled cobalt nanocrystal superlattices [9]. In this paper, we present transmission electron microscopy study of gold coated iron core-shell magnetic nanoparticles and the nanobands assembled under magnetic field.

2 Experiment

The reserve micelle reaction is carried out using cetyltrimethylammonium bromide (CTAB) as the surfactant, octane as the oil phase, and aqueous reactant as the water phase. By varying the water to surfactant ratio ([H_2O]/[CTAB]), we are able to carefully control over the particle size ranging from 5 to 30 nanometers. A co-surfactant of n-butanol is used to help decrease the fraction of the micellar head group that is neutralized and thereby increase the stability of the micelle. Without the addition of the co-surfactant the amount of free water that is available to carry on reactions is greatly reduced as most of the water is locked in the head group of the CTAB. The metal particles are formed inside the reverse micelle by reduction of a metal salt using sodium borohydride. In our experiment we are utilizing the sequential synthesis offered by the reduction of ferrous sulfate

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by sodium borohydride. The iron core is synthesized using two micelle solution with a $\omega = 8$; one with 0.1 M $FeSO_4$(aq), the other with 0.6 M $NaBH_4$ (aq). Both solution are degassed and are mixed together using a magnetic stirrer and under flowing argon. The reaction turns green and then black with the formation of iron nanoparticles within minutes. After the reaction has been allowed to go completion, the micelles within the reaction mixture are expanded to accommodate the shell using a large micelle containing additional sodium borohydride. A micelle solution of $\omega = 10$ was made using 0.1 M $HAuCl_4$. The solution was added almost immediately after the $NaBH_4$ to help prevent the growth of iron nanoparticles *via* Oswalt ripening. The reaction was carried out under short wave UV light and flowing argon. The micelles in the reaction mixture were disrupted using aceton causing nanoparticles to precipitate. Repeated washing using a 1:1 mixture of chloroform/methanol removed the surfactant. The iron containing nanoparticles were separated using a permanent magnet (5000 Oe). The nanoparticles were then dried under vacuum, resulting in a black powder. After passivation with the coating of gold, the particles became air stable with no oxidation detectable in the magnetic data after six weeks.

TEM samples were prepared by ultrasonically dispersing the nanoparticles in acetone for 10 minutes and then dropping them to the carbon grids with filter paper underside to absorb the acetone. TEM samples with nanobands were produced by dropping nanoparticles dispersed in 2 ml toluene and 0.5 ml TOP (trioctylphosphine) on the TEM grid with surface parallel to 0.5 T magnetic field. TEM observation was performed on JEOL 2010 transmission electron microscopy equipped with EDAX DPrime energy dispersive X-ray analysis (EDS).

3 Results and discussion

Fig. 1 is a high magnification micrograph of gold-coated iron nanoparticles. The iron core can be clearly observed. The size and shape of the cores appear unhomogeneous, but very similar to each other. The mean size of the iron core is about 6 nm. The Au shell coated outside of iron can be also seen. The shell is about $1 \sim 2$ nm and well coated on iron core. By focusing electron nanoprobe (2 nm) to the nanoparticles to do EDS analysis, the oxygen peaks were hardly seen, which proved that the nanoparticles were air-stable. If we moved the electron probe to the edge of the nanoparticles, it showed high concentration of gold, which implied gold shell structure formed. Even though the permanent magnet was employed to separate gold-coated iron nanoparticles from gold or incompletely coated iron particles, few such nanoparticles sticking on Fe/Au core-shell nanoparticles could still be observed.

Figs. 2(a) and (b) are selected-area diffraction patterns from pure gold nanoparticles and gold-coated iron nanoparticles, respectively. As gold crystal structure is fcc with lattice parameter $a = 0.408$ nm and Fe is bcc structure with lattice parameter $a = 0.287$ nm, the diffraction rings appear very close to each other as shown in Fig. 2(b). Due to slight mismatch they can be resolved from the broaden diffraction rings of gold 111, 200, 220, 311, and 222 which is caused by overlapping with iron 110, 200, 112, 220, 310, respectively. The separation of two kinds of diffraction rings become much clear at high index diffraction rings such as 220, 311, and 222.

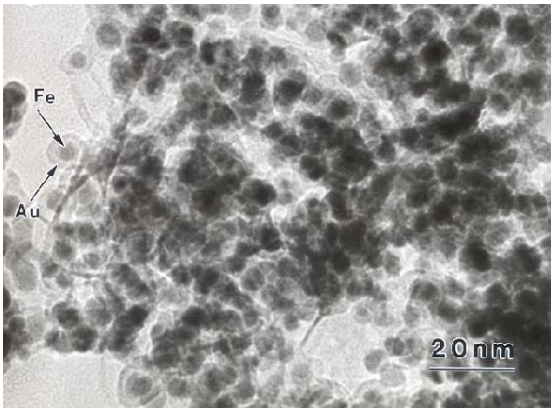

Fig. 1. A TEM micrograph of gold coated iron nanoparticles.

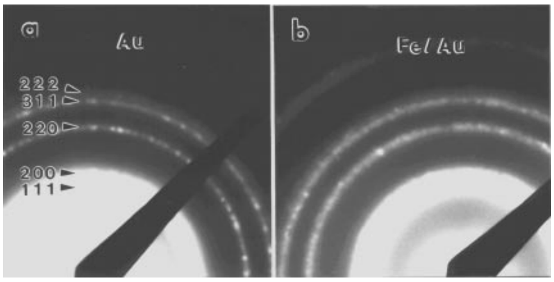

Fig. 2. (a) and (b) are diffraction patterns from pure Au and Fe/Au core-shell nanoparticles.

Fig. 3 is the HREM micrographs of gold-coated iron nanoparticles. In most cases, gold shell lattice can be easily identified and the core of iron appears as dark black in the center of the nanoparticles. The morié patterns were often found in the black iron cores as shown in Figs. 3(a), (b), (c) and (d). The images of the nanoparticles appear different even at the same defocus because of unhomogeneous shapes and different orientations of the nanoparticles.

Generally speaking, the iron core and gold shell should get smaller lattice mismatch as gold shell grows in terms of the orientation relationships of $[100]_{\mathrm{Fe}} \parallel [100]_{\mathrm{Au}}$ and $[010]_{\mathrm{Fe}} \parallel [110]_{\mathrm{Au}}$. Since the iron core grew as sphere-like shape inside reverse micelles, the gold epitaxial growth couldn't perfectly extend to three dimensions. Thus another orientation growth or mismatch could occur during gold shell coating. This is also the reason sometimes we can see morié patterns in the center iron cores in Fig. 3. Until now only those materials with similar structure and close lattice constant presented perfect epitaxial growth in inverted micelle synthesis [10].

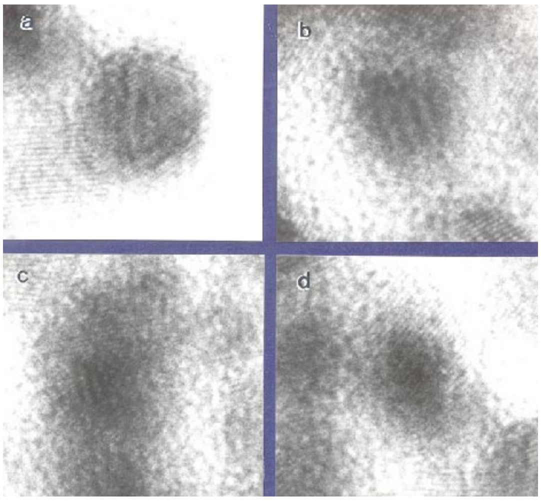

Fig. 3. (a)-(d) are HREM images of gold coated iron nanoparticles.

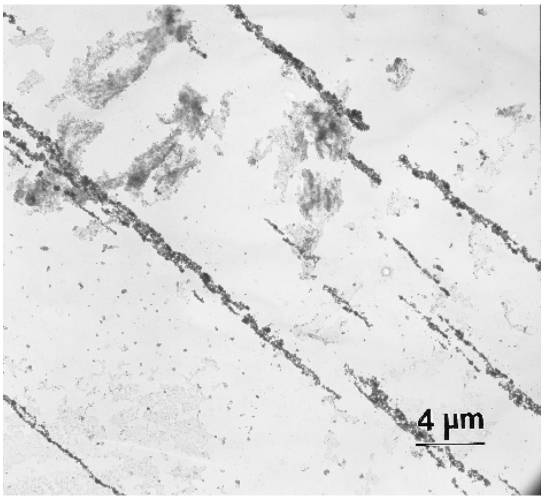

Fig. 5. Nanobands formed by gold coated iron nanoparticles under 0.5 T magnetic field.

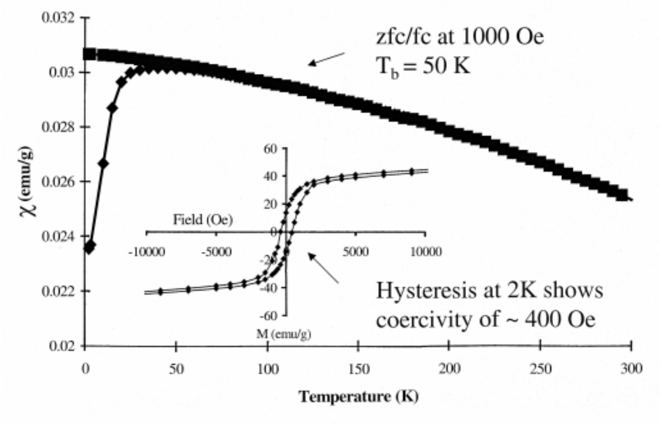

Fig. 4. Magnetic data of gold coated iron nanoparticles.

A representative magnetic susceptibility plot, shown in Fig. 4, exhibits a cusp in the zero field cooled (ZFC) susceptibility at the blocking temperature (T_B). Above T_B, in the superparamagnetic regime, the particles are free to align with the field during the measuring time and depart from the ZFC susceptibility at a temperature near the ZFC maxima and monotonically increases below this temperature. For a superparamagnetic system the blocking temperature is dependent upon the measuring field. The magnetic moment of the particles is 11.5 emu/mol which corresponds to that expected for a bulk iron sample. Below the temperature where the nanocomposites have superparamagnetic behavior, the nanomaterials reveal a remanent magnetization and coercivity. The inset in Fig. 4 shows the magnetization of the gold coated iron sample as the magnetic field of the susceptometer cycles between +50 kOe and −50 kOe. Remanent magnetization (Mr) and coercivities (Hc) for all nanoparticles are 13.67 emu/g and 400 Oe respectively. Above the blocking temperature no coercivity or remanence is observed in the superparamagnetic regime.

Self-assembly is an attractive nanofabrication technique because it provides the means to precisely engineer structure on the nanometer-scale over large sample areas [11]. Recently the spin-dependent tunneling in nanoscale device formed of highly uniformed magnetic-nanocrystal arrays was reported by the electrical measurements [9]. There is a trend to assembly the magnetic nanoparticles to achieve striking magnetic properties for device application. We also tried to assembly the gold coated iron nanoparticles into nanoarrays under magnetic field. Fig. 5 is a TEM micrograph of nanobands formed with gold coated iron nanoparticles. The nanobands were formed parallel to the magnetic field. Some nanobands are longer than 10 μm. The nanoparticles inside the bands are monodispersed. Further attempts are undergoing to assembly these nanoparticles into ordered nanoarrays.

4 Conclusions

Gold-coated iron core-shell structure nanoparticles synthesized using reverse micelles were studied by transmission electron microscopy. The core-shell nanoparticles were successfully synthesized. The average particle size of the core-shell structure is about 8 nm, with about 6 nm diameter core and 1∼2 nm shell. The gold shell structure can be identified from both high resolution electron microscopy and energy dispersive X-ray analysis. Even though the gold and iron electron diffraction rings overlapped a bit, the mismatch of diffraction rings still can be resolved. The magnetic data also shows the successful fabrication of the core-shell magnetic nanoparticles. Though the shell structure coated on the core appear unhomogeneous, nanoparticles stay air stable. The nanobands formed by the nanoparticles under magnetic field were observed by TEM. The nanobands are parallel to the magnetic field. Further study of fabrication two dimensional ordered nanoarrays are undergoing.

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