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# Magnetic properties of assembled ferrite nanostructures induced by magnetic fields

Lixin Zhang, Jia Luo and Qianwang Chen<sup>1</sup>

Hefei National Laboratory for Physical Science at Microscales and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

E-mail: [cqw@ustc.edu.cn](mailto:cqw@ustc.edu.cn)

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## Abstract

Nickel zinc ferrite nanoparticles in the size range of 30–40 nm have been prepared. Coated with polyelectrolyte, the particles were induced to assemble on glass substrates under strong magnetic fields from 0.25 to 0.5 T. The predominant orientation of the assembled chains was observed to be along the direction of the magnetic line of force. As the coating layers increased, ring morphology could be observed. The magnetic properties of the assembled structures were measured and compared to those of ferrite particles prepared without a magnetic field applied.

## 1. Introduction

Because of their small size, nanocrystals generally exhibit properties that differ considerably from those of the bulk solid state [1]. Ordered nanoarrays of magnetic nanoparticles have especially aroused great interest because of their applications in high density magnetic recording devices [2]. In the past few years, several groups have succeeded in organizing magnetic nanocrystals in various mesoscopic structures, such as chains [3], rings [4–6] and 3D superlattices [7, 8]. Magnetic field directed assembly of the magnetic nanoparticles has proved to be an efficient method for obtaining such long range ordered mesoscopic structures, and there have been several studies focusing on the magnetic anisotropy related to sample geometries [9, 10]. In addition to stabilizing nanoparticles against aggregation, organic coating layers on particles have been proved to play an important role in determining the mesoscopic structures and collective magnetic properties [11]. Finely tuning the thickness of the polymer coating is an effective approach for tailoring the magnetic interactions as well as electrostatic forces between particles, which provide a way for further investigating the influence of coating on magnetic properties. In this paper, we demonstrate one-dimensional nanostructures obtained by magnetic field induced alignment of polyelectrolyte coated ferrite nanoparticles.

<sup>1</sup> Author to whom any correspondence should be addressed.

## 2. Experimental section

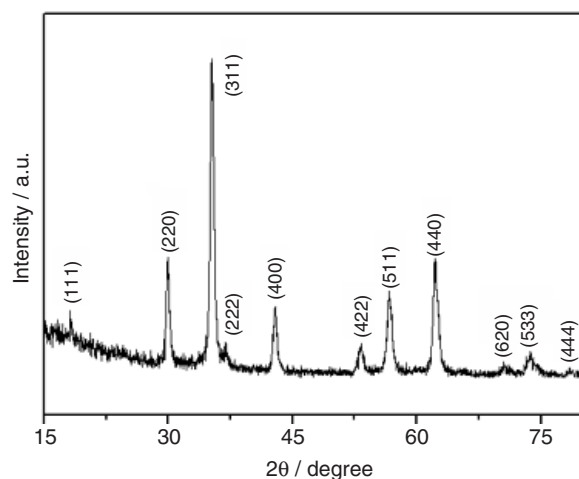
In a typical synthesis, all reagents were of analytical grade and used without any further purification.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in distilled water. Then, this metal salt solution was put into contact with a solution of  $\text{NaOH}$  and  $\text{KNO}_3$ . Upon mixing, ferrite began to precipitate. The aqueous suspension was stirred vigorously before being transferred into a round flask, which was then immersed in an oil bath and kept at  $100^\circ\text{C}$  for 90 min. The product was washed carefully with distilled water and collected with magnets. This washing process was repeated until the pH value of the derived solution decreased to 7. The coating with ferrite particles was performed by LbL (layer-by-layer) deposition of PDA (poly(diallyldimethylammonium chloride)) and PSS (poly(styrenesulfonate)) [12] onto the surfaces of negatively charged NZF (nickel zinc ferrite) particles. In this work, NZF/PE2, NZF/PE3, NZF/PE4 and NZF/PE6 (nickel zinc ferrite coated with 2, 3, 4, 6 layers of polyelectrolytes, respectively) were used for self-assembly in the presence of magnetic fields. The coated particles were dispersed in a solution of 40 wt% aqueous alcohol and the concentration was adjusted to  $0.1 \text{ g l}^{-1}$ . A drop of about  $20 \mu\text{l}$  of the above PE coated ferrite solution was spread on a glass substrate. In the presence of a magnetic field of 0.3 or 0.5 T, the solvent was allowed to evaporate in open air for about 30 min. The structure of the products was analysed using a Rigaku (Japan) D/max- $\gamma$ A x-ray diffractometer equipped with graphite monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The morphologies of ferrite particles were examined by transmission electron microscopy (TEM) using a Hitachi H-800 transmission electron microscope (accelerating voltage = 200 kV). The ferrite nanostructures were examined by scanning electron microscopy (SEM; JEOL JSM-6700F). Thermogravimetric analysis (TGA) was carried out for powder samples with heating and cooling rates of  $10^\circ\text{C min}^{-1}$  using a Shimadzu TGA-50H thermogravimetric analyser in a nitrogen atmosphere up to  $800^\circ\text{C}$ . Magnetic properties were measured at room temperature with a vibrating sample magnetometer (VSM) (Riken Denshi BHV-55) with a maximum applied field of 5 kOe.

## 3. Results and discussion

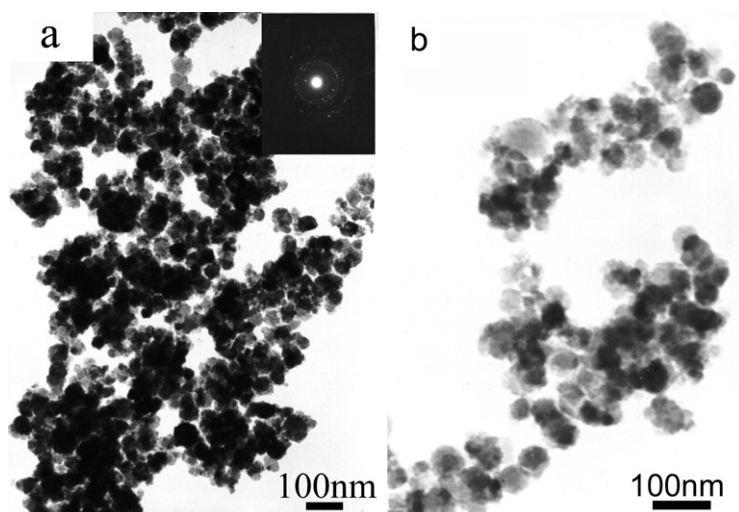
The XRD pattern (figure 1) showed that the sample could be indexed to a nickel zinc ferrite ( $\text{Ni, Zn Fe}_2\text{O}_4$  face-centred cubic phase (JCPDS File No 08-0234). The diameters of the nanoparticles are about 20 nm, calculated from the XRD (311) peak using the Debye–Scherrer formula  $t = 0.89\lambda/(\beta \cos \theta)$ , where  $\lambda$  is the x-ray wavelength,  $\beta$  is the peak width at half-maximum and  $\theta$  is the Bragg diffraction angle.

Figure 2(a) shows the TEM image of the ferrite particles. Particles with size ranging from 30 to 40 nm were clearly observed. The SAED (selected area electronic diffraction) pattern reveals that the particles are well crystallized. Figure 2(b) shows the TEM image of NZF/PE4 particles. It is difficult to identify the core–shell structure from the micrograph possibly because electrons are ready to permeate the shell composed of organic polymer. The average diameter of the coated particles is less than 50 nm since the thickness of every bilayer of PDA/PSS is about 1–2 nm (see table 1 of [12]).

Figure 3 shows the TGA thermograms for uncoated and coated ferrite particles. The first decomposition stage could be assigned to the removal of adsorbed physical and chemical water. The amount of weight loss in this stage increases with increasing amount of adsorbed polyelectrolyte multilayers. This observation is consistent with reported phenomena [13]: the water content functions to stabilize the layer pair. Significant percentage mass losses are recorded during the second thermal degradation stage, between 180 and  $600^\circ\text{C}$ . The weight losses of the four samples are 3.3%, 4.8%, 10.3%, 16.8%, respectively. From (a) and (b), it



**Figure 1.** X-ray powder diffraction pattern of nickel zinc ferrite.

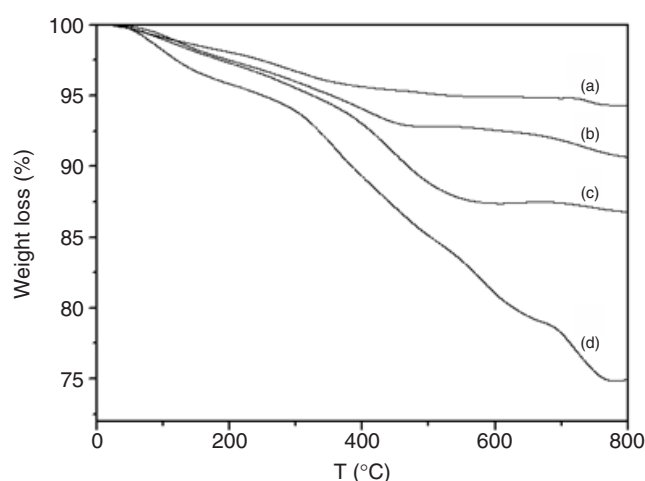


**Figure 2.** TEM micrographs of (a) uncoated  $\text{NiZnFe}_4$  nanoparticles (the inset shows the SAED pattern); (b)  $\text{NiZnFe}_4$  nanoparticles coated with four alternate layers of polyelectrolyte.

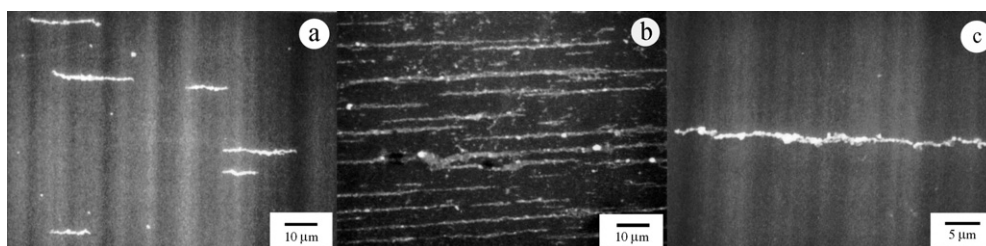
can be deduced that the residuals of the polyanions left are more than those of the polycations after sintering. The weight loss is roughly proportional to the number of layers, so the amount of adsorbed polyelectrolyte multilayers could be estimated from TGA analysis.

Figure 4 shows the SEM images of nanostructures formed by magnetic field induced self-assembly. When the solution of NZF/PE2 was dried in a homogeneous magnetic field, chains with a width of about  $0.5\text{--}0.8\ \mu\text{m}$  and a length of  $20\text{--}80\ \mu\text{m}$  along the direction of the applied magnetic field were formed (figures 4(a), (b)). However, when the solution was dried without a magnetic field, the particles were randomly distributed on the substrate. These results can be explained as follows. The coated particles carry no net magnetic dipole moment in the solution without an applied magnetic field. In this case, particles arranged in a disordered fashion during the solvent evaporation process due to Brownian motion. Homogeneous magnetic fields induce physical torques on ferrite particles. This torque attempts to rotate the particles to align their magnetic moments along the line of force of a magnetic field [14].

The length of the chains is influenced by the strength of the applied magnetic field during the drying process. If the applied field increased from 0.3 to 0.5 T, the length of the chains



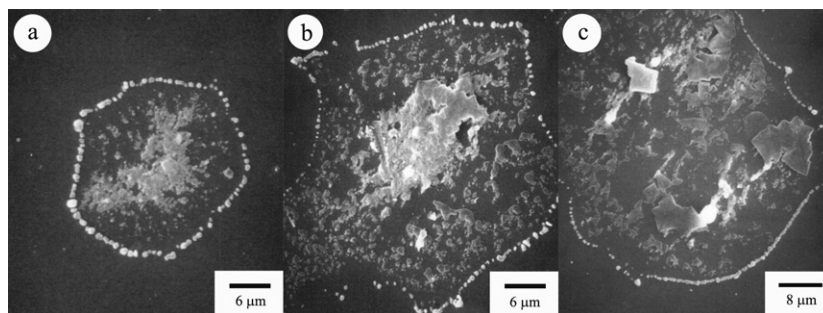
**Figure 3.** TGA thermograms of: (a) NZF/PE1; (b) NZF/PE2; (c) NZF/PE4; (d) NZF/PE6.



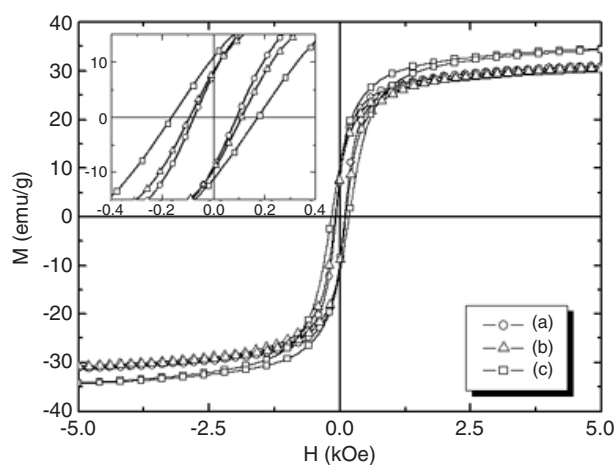
**Figure 4.** SEM micrographs of NZF/PE2 particles deposited on a glass substrate: (a) induced by an external magnetic field of 0.3 T; (b) induced by an external magnetic field of 0.5 T; (c) induced by an external magnetic field of 0.5 T: a magnified image of an NZF/PE2 chain.

increased, from an average of 20  $\mu\text{m}$  to an average of 50–80  $\mu\text{m}$  (figures 4(a), (b)). It is observed that the chains start to form just a few minutes after the application of the magnetic field. As soon as some particles are attracted together, they form a larger dipole moment and create a local inhomogeneous magnetic field, which attracts nearby particles and wires, extending the preliminary chains. This process can be seen in figure 4(c); this longer chain is indeed composed of several shorter ones. The induced dipole moments become greater as the applied magnetic field increases. Thus, as the attraction force between chains is magnified, more particles and chains are held together at the orientation of the external magnetic field. We also performed the same procedures with NZF/PE3 and NZF/PE4 in the presence of a 0.5 T magnetic field, and obtained similar results. The length of the chains did not increase a lot because the strength of the applied magnetic field rather than the coating layers is the major determining factor.

When an NZF/PE6 solution of the same concentration was dried in air with a 0.5 T magnetic field applied, separated ringlike morphologies were observed (figure 5). We attribute this result primarily to the Marangoni effect [5]: hole nucleation in the ultrathin film system occurring due to solvent evaporation. As the solvent that we use is 40 wt% alcohol aqueous solution and the evaporation time is about 1800 s, this system falls in the range of the Marangoni effect (see table 2 of [5]). Once dry holes open up in the liquid film, particles are pushed along the border between the liquid film and solid substrate. Eventually, a sufficient number of particles accumulate along the rim of the opening holes and, subsequently, rings are formed.



**Figure 5.** Several ringlike mesostructures of NZF/PE6 particles, induced by an external magnetic field of 0.5 T (pictures were taken from different regions on the same sample substrate).



**Figure 6.** Hysteresis loops of: (a) uncoated nickel zinc ferrite particles; (b) NZF/PE2 particles not previously induced by a magnetic field; (c) assembly structures of NZF/PE2 particles, induced by a magnetic field of 0.25 T.

When the ferrite particles were coated with excessive polyelectrolyte layers, they were less likely to arrange in line because the oriented flow rate became smaller as the magnetic dipole–dipole interactions were weakened. On the other hand, electrostatic force became a more important factor. Particles are likely to be attracted around the ‘hole centre’ composed of dried ferrite nanoparticle and polyelectrolyte agglomerates. This mesostructure results from the combined influences of above-stated interactions and we are still making experiments to further investigate the proposed mechanism.

To understand the influence of polyelectrolyte coating and applied field on magnetic properties, the hysteresis loops of uncoated and PE coated nickel zinc ferrite nanoparticles (magnetically induced and not) were measured using VSM (figure 6). The coating layers of the samples ranged from one up to six. For magnetically induced samples, a dilute alcohol/aqueous solution of NZF/PE2 was dried in air under a magnetic field of 0.25 T for about 20 h. It could be seen that the coercivity and remanence magnetization are almost the same for the two samples not induced by a magnetic field. The coercivity is about 83.96 Oe for the uncoated sample. On the other hand, the saturation magnetization of the coated sample is slightly smaller than that of the uncoated sample. For example, it can be seen from figure 5 that  $M_s$  for uncoated NZF and NZF/PE<sub>2</sub> takes the values 31.15 and 30.71 emu g<sup>-1</sup> respectively. As the coating layers increased, the saturation magnetization further decreased (results for NZF/PE6 not shown here), because NZF accounts for a smaller moiety in hybridized particles. This is



why the magnetic dipole moment interaction is weakened for NZF/PE6, partially supporting our proposed explanation of ring formation. In comparison, when the same NZF/PE2 particles in solution are induced by a magnetic field first,  $M_s$  increased slightly. We could not attribute this phenomenon primarily to the reduced demagnetization factor  $N_D$  of definite chainlike structure because the saturation magnetization must be independent of the demagnetization factor. The demagnetization factor affects only on the shape of the hysteresis curve. Comparing with that of magnetic nanoparticles [15], it is suggested that the assembly structures formed under a magnetic field should be responsible for the increase of  $M_s$  [16]. On the other hand,  $H_c$  obviously increased to 169.2 Oe. It has been established that for single-domain magnetic particles, the difference in coercivities mainly stems from the magnetic anisotropy energy (MAE). The ferrite particles adopted quasi-one-dimensional aggregates when induced by a magnetic field in advance, and the collective magnetic properties ( $M_s$  and  $H_c$ ) of these nanostructures could be finely tuned by controlled assembly.

#### 4. Conclusions

Chainlike and ringlike nickel zinc ferrite nanostructures were synthesized under magnetic fields by carefully controlling the thickness of the stabilizing reagent of the polyelectrolyte on the surfaces of ferrite particles. It is suggested that only when endowed with adequate magnetization energy could the particles overcome Brownian motion and align along a magnetic line of force. In addition, polyelectrolyte coating layers could effectively prevent the nanoparticles from flocculating by strengthening the electrostatic force between particles as well as adjusting the magnetic dipole interactions. The ringlike structures emerged while thickening the coating polymer as a result of the integrated influence of thermal kinetics, electrostatic force and magnetic dipole interactions.

#### Acknowledgment

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#### References

- [1] Feldheim D L and Foss C A 2002 *Metal Nanoparticles: Synthesis, Characterization, and Applications* (New York: Dekker)
- [2] Martin J I, Noguees J, Liu K and Schuller I K 2003 *J. Magn. Magn. Mater.* **256** 449
- [3] Wiedwald U, Spasova M, Farle M, Hilgendorff M and Giersig M 2001 *J. Vac. Sci. Technol. A* **19** 1773
- [4] Shafi K V P M, Felner I, Mastai Y and Gedanken A 1999 *J. Phys. Chem. B* **103** 3358
- [5] Marllard M, Motte L, Ngo A T and Pileni M P 2000 *J. Phys. Chem. B* **104** 11871
- [6] Tripp S L, Puszty S V, Ribbe A E and Wei A 2002 *J. Am. Chem. Soc.* **124** 7914
- [7] Ngo A T and Pileni M P 2001 *J. Phys. Chem. B* **105** 53
- [8] Legrand J, Petit C and Pileni M P 2001 *J. Phys. Chem. B* **105** 5643
- [9] Petit C, Russier V and Pileni M P 2003 *J. Phys. Chem. B* **107** 10333
- [10] Sahoo Y, Cheon M, Wang S, Luo H, Furlani E P and Prasad P N 2004 *J. Phys. Chem. B* **108** 3380
- [11] Lalatonne Y, Motte L, Russier V, Ngo A T, Bonville P and Pileni M P 2004 *J. Phys. Chem. B* **108** 1848
- [12] Caruso F 2001 *Adv. Mater.* **13** 11
- [13] Farhat T, Yassin G, Dubas S T and Schlenoff J B 1999 *Langmuir* **15** 6621
- [14] Xu X, Majetich S A and Asher S A 2002 *J. Am. Chem. Soc.* **124** 13864
- [15] Wu M Z, Xiong Y, Jia Y S, Niu H L, Qi H P, Ye J and Chen Q W 2005 *Chem. Phys. Lett.* **401** 374
- [16] Niu H L, Chen Q W, Ning M, Jia Y S and Wang X J 2004 *J. Phys. Chem. B* **108** 3996