

Influences of different parameters on the microstructure of magnetic-field-induced self-assembled film

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Abstract. Self-assembled films with needle-like microarrays were fabricated using a mixture of cobalt and fluorocarbon resin under a magnetic field. The various influences of magnetic powder content, viscosity and size distribution on the structure of the self-assembled films were investigated. The self-assembled film morphologies were characterized by stereomicroscope and scanning electron microscopy. Experimental results indicate that an increase in magnetic powder content results in greater unit height and diameter, and that a reduction in viscosity results in increasing array density and decreasing unit width. Additionally, particles with narrow size distribution were able to attain more regular microarray structures. The structural alterations were closely related to numerous effects such as van der Waals forces, dipole-dipole interactions, and external-dipole interactions. The self-assembled film demonstrated magnetic anisotropy, as identified by vibrating sample magnetometry (VSM).

1. Introduction

As a special physical field, the magnetic field demonstrates marked effects on the movement of magnetic particles. In general, magnetic particles as induced by a magnetic field can self-assemble, resulting in a 1D, 2D or 3D structure and morphology [1-4]. It has been reported that self-assembled materials with 3D structures demonstrate more remarkable application prospects in magnetic recording devices, optoelectronic devices, biological sensors, etc. [5-7]. Many researchers have successfully assembled arrays with 3D structures by inducing magnetic fields. However, these structures are typically produced in the magnetic liquid, and are very difficult to maintain once the magnetic field is removed [8-10]. In order to obtain 3D arrays which can be maintained without a magnetic field, needle-like microarrays were fabricated on film surfaces by combining cobalt particles with fluorocarbon (FC) resin [11].

Previous studies have reported that the alteration of parameters such as the strength of magnetic interaction, field strength, or magnetic powder content in a magnetic fluid will result in direct variation of the structural arrangements under a magnetic field [12-15]. Additionally, the present experiment demonstrates that the regulation of parameters may obtain various self-assembled structures. The influence of magnetic field strength on the resulting structure has been previously investigated [11]. In the present research, magnetic powder content, viscosity and particle size distribution were altered in order to investigate the influence of the van der Waals forces, dipole-dipole interactions, and external-dipole interactions on a mesoscopic scale on the microstructure of self-assembled films. The



present investigation provided both fundamental understanding and necessary contributions to potential practical applications. The magnetic anisotropy behavior of films with different applied directions of magnetic field were also studied.

2. Experiment

2.1. Materials

Cobalt (Co) powder was synthesized by chemical vapor deposition. Fluorocarbon (FC) resin with 50% solid content was prepared by the copolymerization of fluorinated monomers. The aliphatic hexamethylene-isocyanate allophanamide (HDI) and cyclohexanone (CYC) were selected for the curing agent and solvent of FC resin, respectively.

2.2. Preparation of self-assembled films

The detailed preprocess was explained in previous literature [11]. The strength of the magnetic field throughout the entire process was controlled at 0.38 T. In the experiment, the viscosities of the assembled solutions were adjusted to 7 mPa s, 14 mPa s, 24 mPa s, 38 mPa s, 63 mPa s and 139 mPa s, respectively, as controlled by the amount of cyclohexanone with a powder content of 0.0072 g/mL. The powder contents were 0.0024 g/mL, 0.0048 g/mL, 0.0072 g/mL and 0.0096 g/mL, respectively, and viscosity was maintained at 38 mPa s. The powder content was equal to the amount of powder divided by the amount of resin. A narrower particle size distribution was obtained by centrifuging the mixture of Co powders, FC resin and cyclohexanone at a rate of 300 r/min.

2.3. Characterization of magnetic powders and self-assembled films

Scanning electron microscopy (SEM, JSM-5900, JEOL) was employed to observe the size and morphology of the Co powder and self-assembled film structures. A stereoscopic microscope (Olympus, BH-2) was also used to observe the self-assembled film structures. The magnetization curve of the magnetic powders and the magnetic anisotropy of the self-assembled films were characterized at room temperature by vibrating sample magnetometry (VSM, ADE-EV7, ADE).

3. Results and discussion

3.1. Influence of magnetic powder content on the structure of self-assembled films

Figure 1 depicts stereoscopic microscopic photographs of the self-assembled films with different Co powder contents, demonstrating the formation of numerous black, needle-like microarrays on the surface of the films, formed by the agglomeration of Co particles. In the present experiment, magnetic particles vibrate, fluctuate, attract one another and form small magnetic clusters under the influence of van der Waals forces during ultrasonic treatment and solvent evaporation. Each magnetic cluster can be regarded as a magnetic dipole, which exhibits larger dipole moments than any single particle. When an external magnetic field is applied, the magnetic clusters in the mixtures tend to arrange in the direction of the magnetic field and aggregate in a chain-like formation, thus forming the microarray structure.

As the content of Co powder increases, the height of the array increases, as well as the mean diameter of single needle structures. When the content reaches 0.0096 g/mL, the microarray disappears and a wall-like aggregation forms. In the system composed of magnetic particles, resin and

solvent, the dominant magnetic dipole forces consist of van der Waals attractions, dipole-dipole interactions and external-dipole interactions [16]. The dipole-dipole interaction energy between two dipoles is given by the following:

$$U = r^{-3}[\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \boldsymbol{r})(\boldsymbol{\mu}_2 \cdot \boldsymbol{r})/r^2] \quad (1)$$

where $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ represent the dipole vectors of dipoles 1 and 2. The dipole moment $\boldsymbol{\mu} = M_s V$, M_s , which represents the saturation magnetization of magnetic particles, and where V is the volume of a single particle, and r is the distance between dipole centers [13].

Alteration of the magnetic powder content results in the variation of r . As the magnetic powder content increases, the distance between particles decreases and the dipole-dipole interactions become stronger. The enhanced resultant force creates longer chains of magnetic particles, which result in thicker, taller needles. Array height increases at a decreasing rate to a certain point, at which the number of chains begins to increase. The chains become so dense that aggregation occurs, as a result of the intensive force between chains.

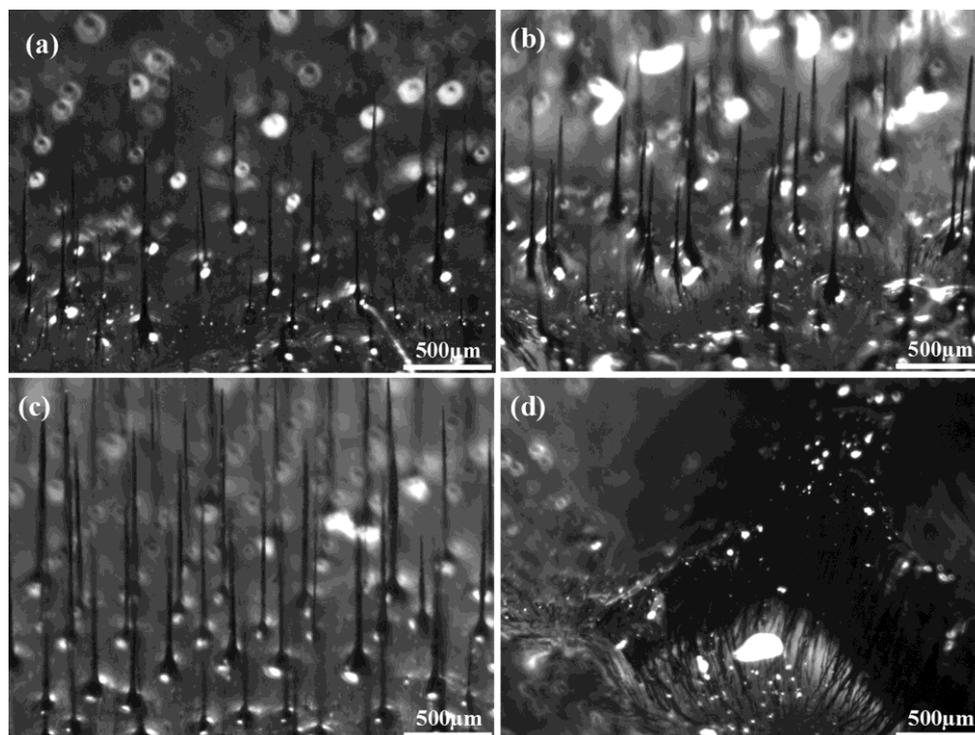


Figure 1. Stereoscopic microscope photographs of Co/FC magnetic-field-induced self-assembled films with Co powder content of (a) 0.0024g/mL (b) 0.0048g/mL (c) 0.0072g/mL (b) 0.0096g/mL.

3.2. Influence of viscosity on the structure of self-assembled films

Figure 2 depicts stereoscopic microscope images of Co/FC self-assembled films. Results indicate that lower viscosity results in denser arrays and smaller needle diameter. As the viscosity increases to 63 mPa s, regular arrays no longer form, resulting in mounded structures with few needles. Further increasing the viscosity results in the elimination of all needles and the appearance of random structural bumps.

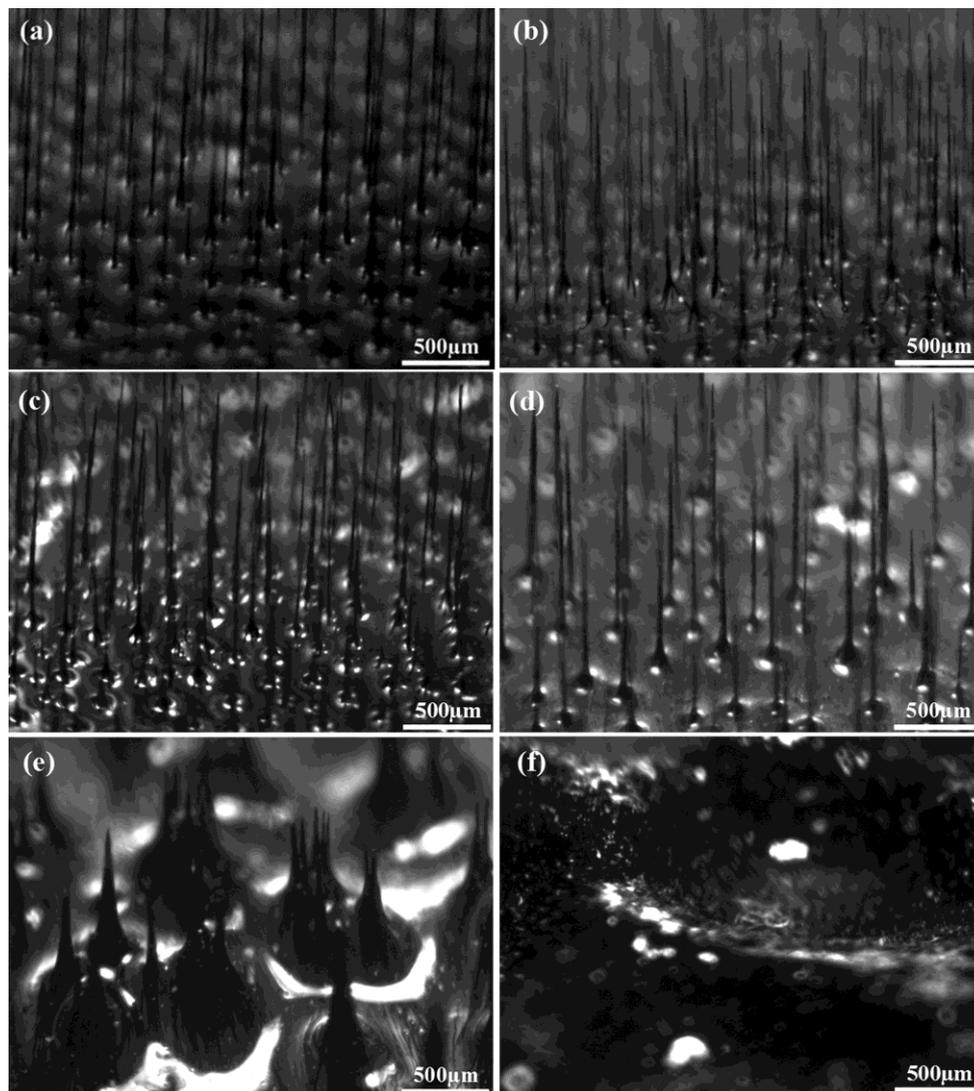


Figure 2. Stereoscopic microscope photographs of Co/FC magnetic-field-induced self-assembled films with viscosity of (a) 7 mPa s (b) 14 mPa s (c) 24 mPa s (d) 38 mPa s (e) 63 mPa s (f) 139 mPa s.

It is generally known that as a result of high molecular weight and viscosity, the presence of polymers will hinder the movement of magnetic particles, clusters and chains. However, the Co particles maintain chain-like arrangements at high viscosities (strong dipole-dipole interactions) under the magnetic field [17]. At higher viscosities, the chains move with greater difficulty and become unevenly distributed, which may result in further aggregation, therefore resulting in larger units. During the self-assembly process, greater repulsion between units results in greater distances between units [18]. The final microarray structures take shape as the result of the balance between the interactions and repulsions between chains. Therefore, viscosity reduction effectively achieves denser arrays and thinner units.

3.3. Influence of particle size distribution on the structure of self-assembled films

The influences of particles size distribution on the microstructural arrays were also studied. The centrifugation of a mixture of Co powder, resin and solvent resulted in narrow particle size distributions. As demonstrated by a comparison of Figure 3(a) and Figure 3(b), the particles demonstrate more uniform size after centrifugation, with identical viscosities and powder contents. The array structures with a narrower size distribution are more regular and the needles are thinner and demonstrate a broader size distribution, as demonstrated by the stereoscopic microscopy and SEM photographs.

Uniform particle volume can result in a uniform dipole-dipole force, resulting in regular structures. Some larger parties exist within the system with broader size distribution, and produce stronger dipole-dipole forces and chain-chain attractions, resulting in thicker arrays.

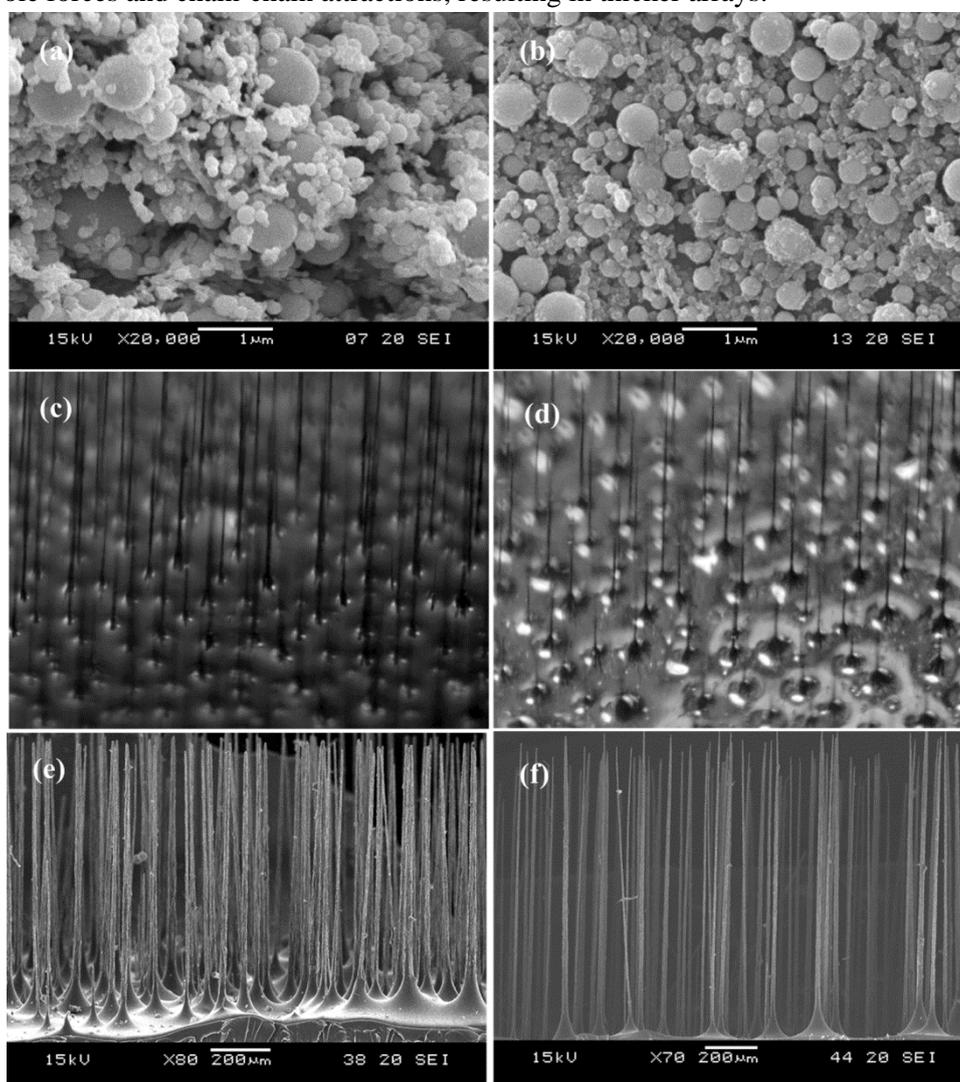


Figure 3. SEM photographs of Co powder (a) without centrifugation; and (b) with centrifugation. Stereoscopic microscopy photographs of magnetic-field-induced self-assembled films formed by Co powder (c) without centrifugation; and (d) with centrifugation. SEM photographs of magnetic-field-induced self-assembled films formed by Co powder (e) without centrifugation; and (f) with centrifugation.

3.4. Magnetic properties

The hysteresis loops of the self-assembled films are depicted in Figure 4. The shapes of the two hysteresis loops presented in the figure differ from one another when the magnetic field is applied perpendicular or parallel to the plane of the film. The film with a perpendicular applied field demonstrates greater saturation magnetization than that under the influence of a parallel applied field. The reduced remanence (M_r/M_s) of Co is 0.074 when the applied field is perpendicular to the film plane, whereas the reduced remanence is 0.033 when the applied field is parallel to the film plane. Based on the results described above, the arrays growing in the direction perpendicular to the film plane can be easily magnetized. During the self-assembly progress, partial magnetic particles rotate to arrange with the field applied along the easy axis, resulting in the magnetic anisotropy of the self-assembled films [10].

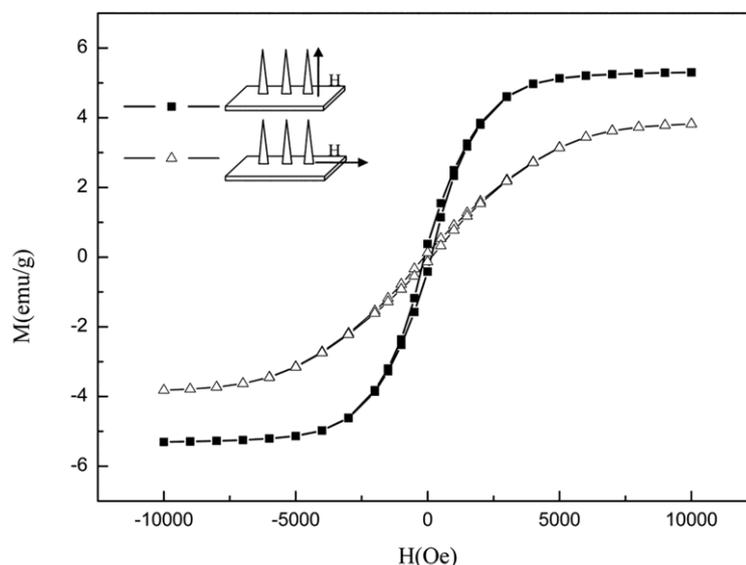


Figure 4. Magnetic hysteresis loop of self-assembled films under magnetic fields applied in different directions.

4. Conclusion

Cobalt was used to assemble microarrays under magnetic fields. Experimental results indicate that the particle volume and saturation magnetization of the magnetic particles had great influence on the self-assembled film structures. Increasing magnetic powder contents resulted in taller microarrays comprised of larger units, while reduction in viscosity resulted in denser arrays comprised of thinner units. The narrower size distribution of particles was easily to get more regular microarray structures. The different shapes of magnetic hysteresis loops and the alteration between reduced remanences (M_r/M_s) measured under different magnetic field directions demonstrated the magnetic anisotropy of the self-assembled films.

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