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Quasi-One-Dimensional Assembly of Magnetic Nanoparticles Induced by a 50 Hz Alternating Magnetic Field

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The control of assembly from building blocks into ordered structures is a promising and interesting issue in nanoscience and nanotechnology. Recently, we reported that alternating magnetic field of tens of kHz can induce the fibrous assembly of magnetic nanoparticles[1] and the formation of discrete particulate monolayers of non-magnetic nanoparticles.[2] However, in daily life, there is another important alternating magnetic field, namely power–frequency alternating magnetic fields. This is because the human body is exposed to this field at all times (consider power lines and electric appliances). Therefore, the study of colloidal behavior under such a field is vital to the biomedical applications of magnetic nanoparticles. Moreover, the investigation of assembly under low-frequency alternating fields also plays a role in the study of frequency responses of nanoparticle assembly, which is vital to understanding the mechanism. According to the Maxwell–Faraday equation [Eq. (1)]:[3]

$$\nabla \times E = -\frac{\partial B}{\partial t} \quad (1)$$

the time-varied magnetic field generates a circular electric field around the nanoparticles that is proportional to the frequency of alternating magnetic field.

Herein, we describe the development of a 50 Hz alternating magnetic field generator and employed this field to assemble the magnetic nanoparticles. 50 Hz is the power frequency of China and the equipment is easy to produce.

The magnetic field was sinusoidally dependent and generated by a solenoid of 800 turns with iron oxide as ferrocore (Figure 1 a). The driving voltage was supplied by a power convertor. The cross section of ferrocore was 30 mm × 30 mm. The solenoid contained a 20 mm gap. In experiments, the samples were placed in the middle of gap and can be parallel (Figure 1 b) or perpendicular (Figure 1 c) to the field. According to Ampere's circulation theorem, the magnetic field intensity inside the gap can be determined by Equation (2):

$$NI = Hl \quad (2)$$

where N is number of turns, I is the excitation current, H is

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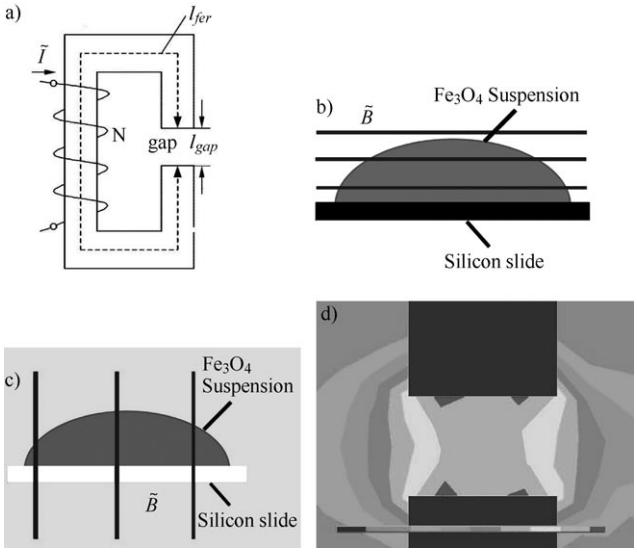

Figure 1. Experimental configuration and the generated magnetic field. a) The gap in the device where the magnetic field is generated. d) Simulated distribution of the magnetic field intensity. The area under the curve and the horizontal lines indicate minimal and maximal field intensities, respectively. Experimental configuration: the field is b) horizontal and c) perpendicular to the substrate and is distributed as in (d).

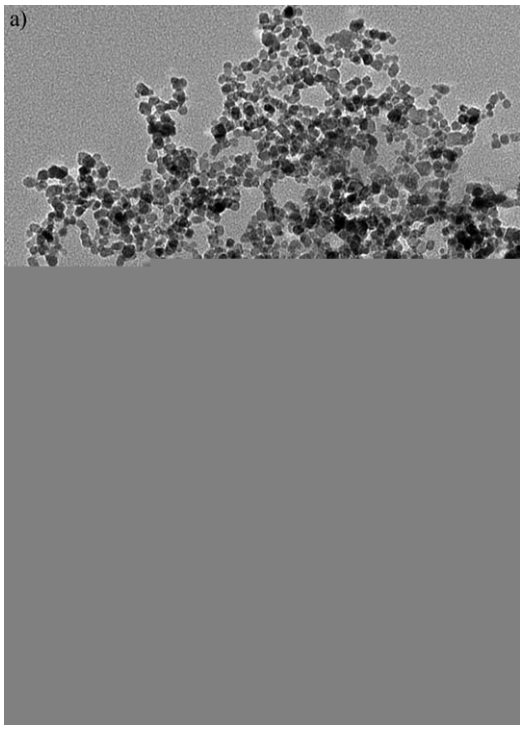

Figure 2. a) TEM image of Fe_3O_4 nanoparticles dispersing in superpure water. b) Corresponding particle-size histogram of Fe_3O_4 nanoparticles.

magnetic field intensity, and *l* is the width of gap. The simulative distribution of the magnetic field is presented in Figure 1 d. From the simulative distribution of field, the field is uniform in the middle of the gap.

In the experiments, the diameter of nanoparticles was about 10–11 nm and they were polydispersed (Figure 2). VSM measurements showed that the nanoparticles were superparamagnetic. In the absence of any magnetic field, the magnetic nanoparticles formed amorphous aggregates due to solvent evaporation (Figure 3 a). However, in the presence of the vertically applied alternating magnetic field, the Fe_3O_4 nanoparticles formed fibrous assemblies, which should consist of massive Fe_3O_4 nanoparticles.[1] As the field intensity increased, the width of the assemblies decreased from 2.25 μm to 1.17 μm (Figure 3 g) and their length increased from 34.04 μm to 73.74 μm on average (Figure 3 h). There was a remarkable transition from amorphous aggregates to fiber-like assemblies (Figures 3 b–f).

Traditionally, magnetostatic fields have often been used to direct the assembly of nanoparticles, generally resulting in wire- or chain-like structures.[4] The mechanism was magnetic dipolar interaction. The nanoparticles formed head-to-tail structures to minimize the systematic energy. However, if the magnetostatic field was vertical to the assembly substrate, the nanoparticles formed separated isotropic structures due to the parallel moments repulsion.[5] Our results were different from both cases, as the field was vertical to the assembly plane but the structures were fibrous. This was in accordance with the results previously reported.[1]

We additionally made the assembly experiments with the field parallel to the assembly plane to see the effect of field direction. When the alternating magnetic field was exerted parallel to the substrate, the Fe_3O_4 nanoparticles aggregated into straight and long micro-chains. Different from those mentioned above, the width and length both increased with the field intensity. The width increased from 1.72 μm to 4.43 μm and the length increased from 46.6 μm to 247.2 μm on average (Figure 4).

We measured the magnetic property of three samples—naturally-dried aggregates, assemblies under a vertically applied magnetic field and assemblies under a parallel applied magnetic field. The VSM measurements are presented in Figure 5. As shown in Figure 5, after the treatment of alternating magnetic field, the assemblies remain superparamagnetic, but the saturated magnetization decrease. It is an interesting result, because the fact that the assemblies remain superparamagnetic shows that there is scarcely quantum exchange between the nanoparticles. However, the fact that the saturated magnetization of field-mediated assemblies is below that of the naturally dried aggregates reveal that it is harder to magnetize the field-

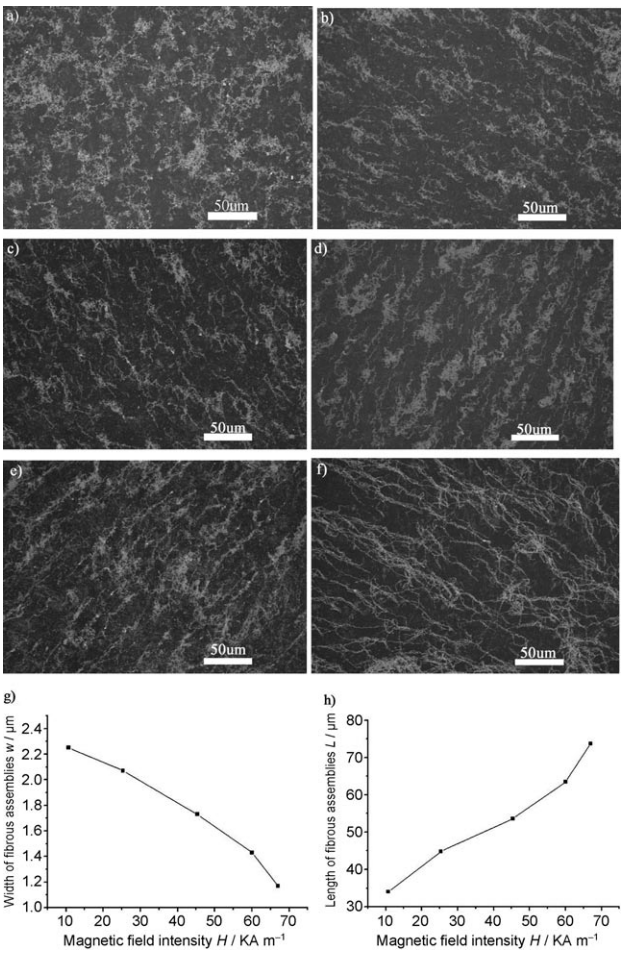

Figure 3. a) SEM image of Fe_3O_4 nanoparticles aggregates after natural solvent evaporation. b)–f) SEM images of Fe_3O_4 nanoparticles assemblies in the presence of a vertically applied alternating magnetic field. The field intensities are b) 10.67 KA m^{-1}, c) 25.33 KA m^{-1}, d) 45.33 KA m^{-1}, e) 60 KA m^{-1}, f) 72 KA m^{-1}. g) Length and h) width of the assemblies versus field intensity.

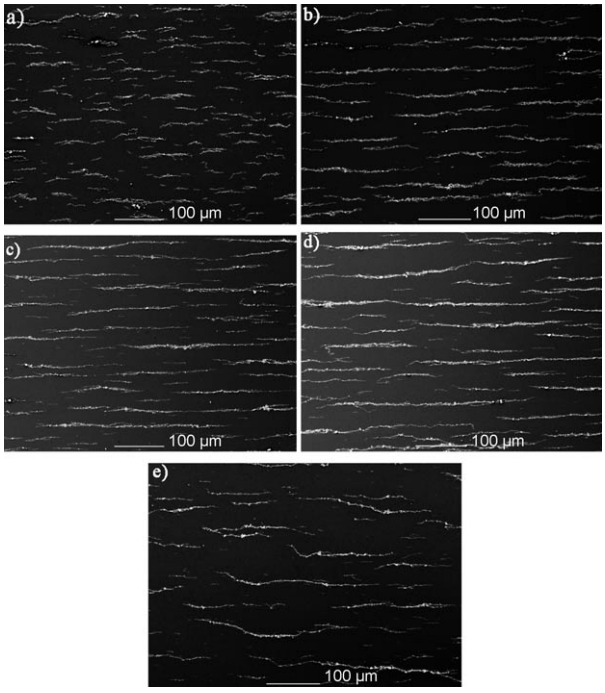

Figure 4. SEM images of Fe_3O_4 nanoparticles assemblies in the presence of parallel-applied alternating magnetic field. The field intensities are a) 10.67 KA m^{-1}, b) 25.33 KA m^{-1}, c) 45.33 KA m^{-1}, d) 60 KA m^{-1}, e) 72 KA m^{-1}.

treated samples than to magnetize the naturally dried sample in the direction vertical to the substrate (anisotropy).

By comparing aggregating patterns, the conformation of aggregates under the parallel alternating field is similar to that under the parallel magnetostatic field. However, the assembly pattern under the perpendicular alternating magnetic field is actinomorphous (Figure 6), which shows that the magnetic force mediates the anisotropic assembly on the basis of isotropic solvent evaporation.[6] The possible mechanism of assembly is schematically shown in Figure 7. The magnetic moments of the particles can be induced by the external magnetic field. In the presence of the parallel applied magnetostatic field,[7] the particles form head-to-tail structures

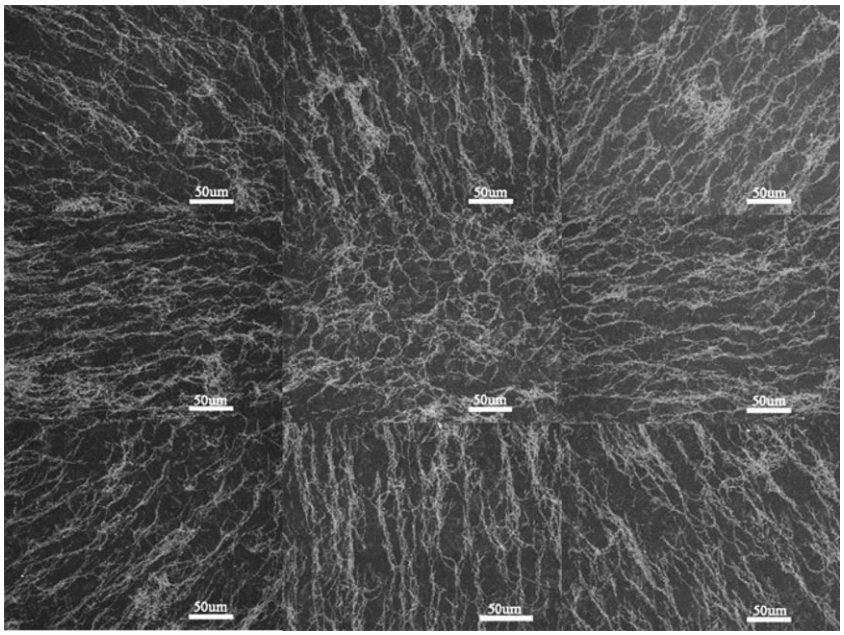

Figure 6. Effect of solvent evaporation on the assembly pattern. The nine images show an actinomorphous pattern of assembled fibers in a certain area. The field is applied vertically to the substrate and the intensity is 72 KA m^{-1}.

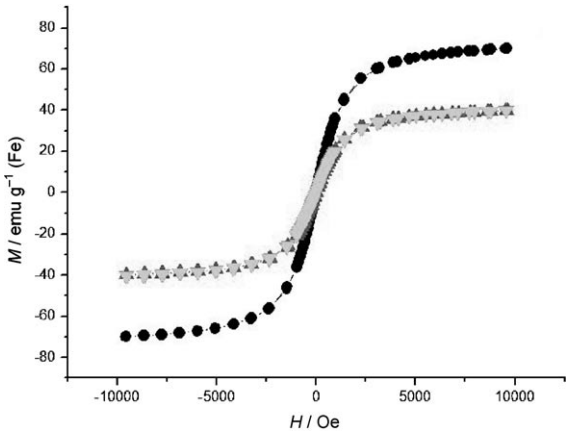

Figure 5. Hysteresis loops of Fe_3O_4 nanoparticles after natural drying (●), the treatment of the vertically applied (▲) and parallel applied (▼) alternating magnetic fields. Hysteresis loops of Fe_3O_4 nanoparticles after vertically applied (▲) and parallel applied (▼) alternating magnetic fields coincide with each other closely.

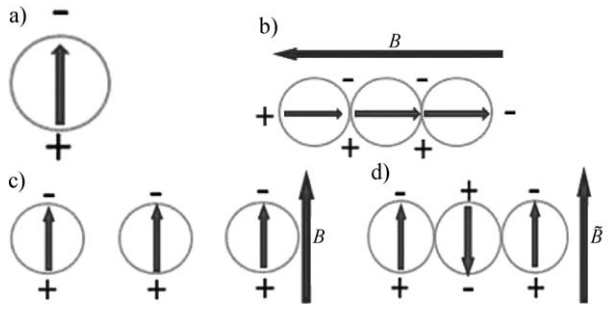

Figure 7. Possible mechanism of assembly. a) The cluster is modeled as a dipole (a dipole can be considered as a couple of magnetic charges). b) In the presence of a parallel applied magnetostatic field, the particles form head-to-tail structures. In the case of the parallel-applied alternating magnetic field, the result is similar. c) In the presence of the vertically applied magnetostatic field, the dipolar moment is parallel and the force of interaction is repulsive. d) In the presence of the vertically applied alternating magnetic field, the dipolar moment varies with the external field. When the dipolar moment is anti-parallel, the interacted force is attractive.

(Figure 7 b) to minimize the systematic energy. In the presence of the vertically applied magnetostatic field, the dipolar interaction causes a repulsive force among the particles because the dipolar moments are parallel. In the presence of the vertically applied alternating magnetic field, the magnetic moments vary with the external field. The relaxation time is given by Equation (3):[8]

$$\tau_B = \frac{4\pi\eta r^3}{kT} \qquad (3)$$

where η is the basic liquid viscosity, r the hydrodynamic radius of the particle, k Boltzmann's constant, and T is thermodynamic temperature. With the evaporating of solvent and shrinkage of the liquid surface, the suspension viscosity becomes greater and the clusters also become larger, which increases the relaxation time [Eq. (3)]. When the relaxation time is equal to or greater than 20 ms, the magnetic moments inside the clusters will not follow the variety of the external field, which may cause the anti-parallel magnetic moment's magnetic interaction. In the presence of the parallel applied alternating magnetic field, the mechanism may be similar to that of the mag-

netostatic field. However, the magnetic force of the parallel applied alternating magnetic field on nanoparticles was half of that of the magnetostatic field on nanoparticles.[9]

In summary, we developed a 50 Hz alternating magnetic field generator that was easy to produce and convenient to use. Moreover, we have demonstrated that the low-frequency alternating magnetic field perpendicular to the substrate can induce the fibrous assembly of magnetic nanoparticles like a high-frequency magnetic field, but different from the hexagonal and labyrinthine types reported previously.[10] Under the low-frequency alternating magnetic field, the assemblies remained superparamagnetic. We believe our preliminary work will provide further understanding of the assembly process in future research, especially in the cell research, such as the interaction between morphological surfaces and interfaces and cells.

Experimental Section

The silicon slides were cleaned by a hot mixture of H_2O_2 and H_2SO_4 (with volumetric ratio of 3:7). Before each experiment, the sample was ultrasonically dispersed for 10 min, and the suspension solution was stable for about 24 h, which was sufficient for our experiment. After ultrasonically treated for 10 min, the as-synthesized suspension solution (about 5 μL) was spread on a silicon slide and subjected to the alternating magnetic field.

Synthesis of Fe_3O_4 Nanoparticles: Magnetite (Fe_3O_4) nanoparticles of 10–11 nm were prepared by mixing a solution of $FeCl_3$ and $FeSO_4$ (molar ratio 2:1) dissolving in 2 mol L^{-1} HCl solutions, followed by slowly adding 1.25 L 12.5% (w/w) $N(CH_3)_4OH$ under stirring.[11] When vigorous stirring was continued about 30 min, a black precipitate can be obtained. The precipitate can be isolated by the application of a permanent magnet and washed by use of superpure water. To remove the excess Fe and others, the above process should be repeated six times. Finally, the precipitates were dispersed in superpure water to form suspension solution. The Fe content in final suspension was about 12.9 μg mL^{-1}, and pH value of the suspension was approximately 7.[12]

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Keywords: alternating magnetic fields · colloids · magnetic properties · nanoparticles · self-assembly

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[9] The magnetic force of a magnetic nanoparticle under a static magnetic field can be expressed by:

$$F = \frac{V\Delta\chi}{\mu_0}(B\nabla)B \quad (1)$$

where V is the volume of the particle, $\Delta\chi$ is the difference in the magnetic susceptibilities of the particle, μ_0 is the vacuum permeablility, B is the magnetic field strength and ∇ is the field gradient. If the field is alternating or time-varied, the B should be replaced by $B\sin\omega t$. Thus, Eq. (1) becomes

$$\tilde{f}_{mag} = \frac{V\Delta\chi}{\mu_0}(B\nabla)B\sin\omega t = \frac{V\Delta\chi}{\mu_0}(B\nabla)B\left(\frac{1-\cos 2\omega t}{2}\right)$$

During the whole period, the second term is zero. Moreover, $\tilde{f}_{mag} = \frac{1}{2}f_{mag}$, if the amplitude maximum of alternating magnetic field equals the intensity of the magnetostatic field.
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