

Fibrous Aggregation of Magnetite Nanoparticles Induced by a Time-Varied Magnetic Field**

Jianfei Sun, Yu Zhang, Zhongping Chen, Jie Zhou, and Ning Gu*

Assembly of building blocks into more complex structures holds promise for both theoretical research and technological applications.^[1] To control or modulate the assembled structures, physical forces, such as electric or magnetic fields, are often employed.^[2] This combination of “bottom-up” and “top-down” techniques is a rapidly growing field, however, there have been few reports on the relationship between the assembled conformation and the features of the building block. In particular, in field-assisted assembly, wirelike structures are generally obtained as a result of the induced dipolar effect,^[3] which makes the features of the building block hard to visualize due to conformational variations.

We believe that the augmentation of field complexity may help to resolve this problem.^[4] Herein, it is demonstrated that a time-varied magnetic field is capable of inducing magnetite (Fe_3O_4) nanoparticles (building blocks) to form fibrous aggregates, and of mediating the morphological diversity of assembly that is controlled by colloidal surface charge.

Oleic acid capped Fe_3O_4 nanoparticles were first prepared by following the procedure reported by Peng et al.^[5] Then the colloidal surfaces were chemically modified with 3-aminopropyltriethoxysilane (APTS; $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$) to form an aqueous solution. This process was briefly described in reference [6]. The Fe content in the final colloid was about $28 \mu\text{g mL}^{-1}$ and the pH value of the suspension was approximately 7. After ultrasonic treatment, the final colloid was stable for about 36 h, and before each experiment the sample was ultrasonically dispersed for 10 min.

The as-synthesized colloidal solution (about 20 μL) was spread on a silicon slide and subjected to an alternating-current magnetic field. The field was generated by a five-turn coil that was energized by a high-frequency power supply. For its industrial purpose, the frequency was fixed at about 80 kHz. In contrast to conventional experimental configura-

tions, the field was sinusoidally time-dependent and its direction was normal to the assembly plane. The conceptual scheme is illustrated in Figure 1.

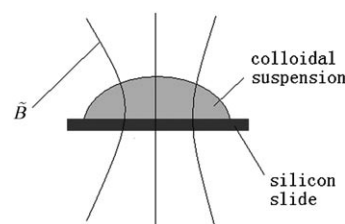


Figure 1. Experimental configuration: the field is perpendicular to the substrate and is sinusoidally time-dependent.

In the absence of a time-varied magnetic field, solvent evaporation results in amorphous aggregation of nanoparticles (see Figure 2a).^[7] However, when a time-varied magnetic field is applied, the Fe_3O_4 nanoparticles aggregate into mesoscale fibers that are several micrometers wide and several hundreds of micrometers long (see Figure 2b). Based on the magnification of a localized area, the fibers consist of massive Fe_3O_4 nanoparticles. In addition, at increasing field intensity the transition from a fiberlike conformation to an amorphous conformation can be observed (see Supporting Information). Hence, the higher field intensity does not favor one-dimensional assembly, in contrast to previous reports where a stronger field leads to improved assembly.

Moreover, the collective magnetic properties (Figure 3) reveal that the fibrous aggregates have a common magnetism with individual nanoparticles (the 10-nm Fe_3O_4 nanoparticle is superparamagnetic), whereas such magnetic structures previously prepared by magnetostatic-field-assisted assembly show a ferromagnetic behavior.^[8] The superparamagnetism of the particulate ensemble reflects the loose contact between nanoparticles, so that the distance between two magnetic moments is too large to permit the quantum-exchange mechanism to work (Heisenberg model).^[9]

The above-mentioned phenomenon is reproducible for other surface coatings, such as dimercaptosuccinic acid (DMSA; $\text{HOOCCH}(\text{SH})\text{CH}(\text{SH})\text{COOH}$), tartaric acid, and glutamic acid. However, for oleic acid capped Fe_3O_4 nanoparticles (dispersed in toluene), the fibrous assembly is not observed.^[10] Instead, very short chains consisting of tens of nanoparticles are found, which reveals that massive aggregation of nanoparticles does not occur and only magnetic dipolar interaction plays a role in the formation of very short chains. As a result of the very small volume of the nanoparticles, the magnetic dipolar interaction is also very weak

[*] Dr. J. Sun, Prof. Dr. Y. Zhang, Dr. Z. Chen, Dr. J. Zhou, Prof. Dr. N. Gu
State Key Laboratory of Bioelectronics and
Jiangsu Provincial Key Laboratory of Biomaterials and Biodevices
School of Biological Science and Medical Engineering
Southeast University, Sipailou 2, Nanjing (China)
Fax: (+86) 258-379-4960
E-mail: guning@seu.edu.cn
Homepage: <http://www.lmbe.seu.edu.cn/nano>

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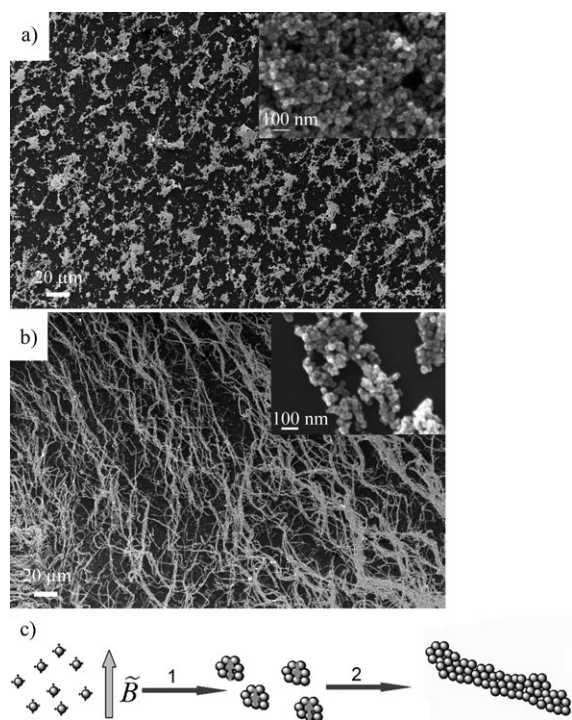


Figure 2. a) Scanning electron microscopy (SEM) image of Fe_3O_4 nanoparticle aggregates after solvent evaporation in the absence of an alternating-current magnetic field. Inset: Magnified image. b) SEM image of pattern formation of electrostatically stabilized Fe_3O_4 nanoparticles under an alternating-current magnetic field. The excited current is 170 A, which is the minimum of our equipment. For subsequent magnetic property measurement, the concentration is higher than $28 \mu\text{g mL}^{-1}$, at approximately 0.5 mg mL^{-1} . c) Formation of microfibers from an electrostatically stabilized colloidal suspension under an alternating-current magnetic field. 1) Breakdown of electric double layer leads to aggregate formation; alternating magnetic field destroys the electric double layers. 2) There exist parallel or antiparallel magnetic moments inside clusters; dipolar attraction leads to the formation of meso-fibers.

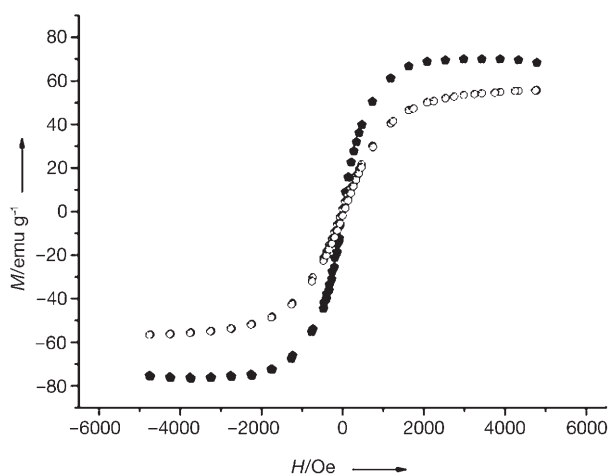


Figure 3. Hysteresis loops of Fe_3O_4 nanoparticles after conventional drying (●) and after time-varied magnetic-field-induced drying (○).

between nanoparticles, and the strong repulsion of oleic acid molecules prevents the formation of long chains. Therefore, the formation of clusters is crucial to the microscale fiberlike aggregation. Noticing that the former are electrostatically stabilized while the latter is sterically stabilized, we inferred that the assembly is not only induced by magnetic dipolar effects but also depends on the electrostatic interactions.

According to Faraday's law of electromagnetic induction, the time-varied magnetic field will induce a rotating electric field around the nanoparticles. As for electrostatically stabilized nanoparticles, the colloidal electric double layers will interact with the rotating electric field, which resembles the case of an electromagnetic wave passing through a spherical capacitance. Clearly, the induced electric field will deform the electric double layers and weaken the colloidal stability, thus leading to the amorphous aggregation of small particles (Figure 2b, inset).^[11] With the clusters growing larger, the internal magnetic moments are simultaneously enhanced and oscillate with the external magnetic field. As the particulate relaxation time is positively proportional to the cube of the particle size,^[12] the relaxation time of the clusters increases to be comparable to the period of the external time-varied magnetic field. Thus, the directions of the moments inside different clusters may well not be identically synchronous with the external field. If the moments inside neighboring clusters are antiparallel, the magnetic force between the two moments is attractive (parallel magnetic moments generate a repulsive force).^[13] The attractive force brings two clusters together and further induces the formation of microfibers because of the anisotropic dipole moment interaction (see Figure 2c). With increasing field intensity, the induced electric field is also enhanced and can polarize the colloidal surfaces to generate polarized charges. Therefore, the isotropic electrostatic interaction between particles tends to predominate over the anisotropic magnetic moment interaction, which results in the conformational transition from a chainlike assembly to amorphous aggregation.

Based on the above-mentioned hypothesis, Fe_3O_4 colloidal solutions of various ζ potentials were studied experimentally under a fixed external field. The ζ potential was adjusted by changing the pH value of the colloid by dropwise addition of 0.1 M HCl or NaOH solution. The relationship between pH value and ζ potential is plotted in Figure 4a; the SEM images of the corresponding conformations are presented in the Supporting Information. Here, noticing that there is a clear difference in ζ potential between pH 7 and 7.5, the SEM images of the corresponding assemblies are also included in Figure 4b and c. It can be seen that their conformations are significantly dissimilar, although the pH values are nearly the same. Notably, the isoelectric point of the colloidal suspension (where the absolute value of the ζ potential is minimal) is located where the pH value is about 7. Also, we find that it is just at pH 7 that the best-assembled conformation emerges, which manifests the mesoscale order and periodicity of fibers (Supporting Information). With the absolute value of ζ potential increasing (toward alkaline or acidic conditions), the assembled patterns both become amorphous. The electrostatic interaction may well account for this effect. The higher

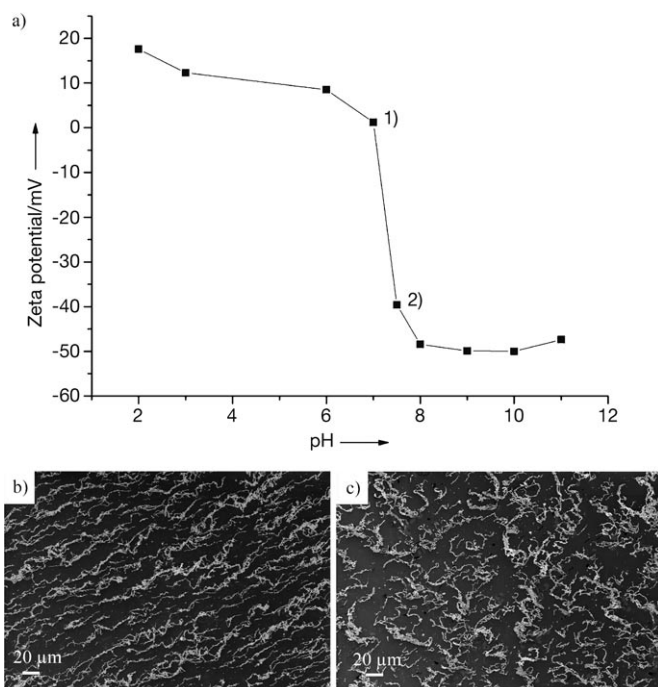


Figure 4. a) Plot of ζ potential versus pH value; 1 and 2 indicate samples with significantly different ζ potentials. b,c) Conformational SEM images of samples 1 and 2, respectively. The alternating-current magnetic field is present and the excited current is 200 A.

ζ potential means there are more charges on the particulate surfaces, which generate stronger electrostatic interactions that provide repulsive forces against the attractive magnetic moment interactions.

By associating the results with the correlation between assembly and field intensity, we conclude that the fibrous assembly of Fe_3O_4 nanoparticles results from the competition between the surface-charge-controlled electrostatic interaction and the external-field-induced magnetic moment interaction. Only the time-varied magnetic field connects the two interactions, thus making the assembled conformation possible to visualize by the variation of both interactions.

As this work was in progress, Alivisatos and co-workers reported the direct-current electric-field-induced self-assembly of nanorods.^[14] It is our next challenge to exploit alternating-current magnetic fields in the assembly of anisotropic particles. It is interesting to make a comparison between their work and ours. In the report by Alivisatos et al., the electric field is static and its role is to align the moment of the nanorods perpendicularly (because of the shape anisotropy, the nanorods are also aligned perpendicularly to the substrate). In our experiments, the magnetic field is time-varied and the role of the field is to drive nanoparticle assembly by a combination of electrostatic interaction and magnetic moment interaction. Moreover, the self-assembly of the nanorods is mediated by solvent evaporation, whereas the assembly of nanoparticles is independent of solvent drying because the Fe_3O_4 nanoparticle aggregates can be observed in solution by optical microscopy. Finally, the self-assembly in the work of Alivisatos et al. produces superlattices of nano-

rods, while the field-assisted assembly in our work gives rise to superstructures of nanoparticles.

In summary, we have demonstrated the alternating-current magnetic-field-induced diverse assembly of magnetite nanoparticles that is in close relationship with the surface charge. We believe our preliminary work will provide further understanding of the assembly process in fundamental research. Also, the time-varied magnetic field, as a novel tool for manipulating magnetic materials, should be paid more attention in the future.

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With this modification, the evaporation of toluene is slowed and approximates to that of water.

- [11] This observation can be partially confirmed by the effect of an alternating magnetic field on a Au colloidal solution, which was another project in our laboratory. If a vial of Au colloidal solution was subjected to an alternating magnetic field, the color of the suspension turned from red to blue quickly when the field intensity was high enough.
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