Low-field-induced spin-glass behavior and controllable anisotropy in nanoparticle assemblies at a liquid-air interface

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ABSTRACT Stacking nanoscale-building blocks into one-dimensional (1D) assemblies with collective physical properties is a frontier in designing materials. However, the formation of 1D arrays using weak magnetic fields and an in-depth understanding of their magnetic properties remain challenging. Here, low-dimensional assemblies of iron oxide nanocubes with a disordered arrangement are fabricated at the diethylene-glycol/air interface in the presence of assembly fields (0/1/3/5/30/50 mT). Ring-shaped assemblies gradually transform as the assembly field increases from 0 to 50 mT, first to a porous network consisting of elongated assemblies and then to an aligned array of filaments, in which the aligned filaments are formed when the assembly field is ≥ 3 mT and duration $t > 14$ min. Spin-glass characteristics and static (dynamic) anisotropy factors $\sim 2(3)$ are achieved by tuning the strength of the assembly field. In the presence of a relatively weak assembly field, the interplay between dipolar interactions and disorder with respect to magnetic easy axis alignment leads to spin-glass characteristics. The alignment of the magnetic easy axes and the strength of the dipolar interactions increase with increasing assembly field, resulting in the disappearance of spin-glass characteristics and enhancement of the magnetic anisotropy. This study presents a strategy for obtaining magnetic assemblies with spin-glass behavior and controllable anisotropy while shedding light on the magnetic interactions of low-dimensional assemblies.

Keywords: magnetic nanoparticles, assembly, anisotropy, spin glass

INTRODUCTION

Magnetic nanoparticles and assembled nanostructures have been widely applied in science and technology due to their unique magnetic properties, biocompatibility, and low efficiency. Nowadays, nanoparticles produce assembled nanostructures of various shapes, including spheres, cubes, rods, and tetrapods, with a wide range of array sizes, shapes, and arrangements. The interest in iron oxide nanoparticles, one of the most studied magnetic nanoparticles, is mainly focused on their application in the field of biomedicine [1,2], e.g., magnetic biosensing [3,4],

immunoseparation [5], magnetic particle imaging [6], targeted drug delivery [7], and magnetic hyperthermia therapy [8]. Moreover, iron oxide nanostructures are also used in other applications, such as magneto-responsive devices [9], flexible magnetic actuators [10], and electromagnetic devices [11]. Assembly or aggregation of such building blocks yields complex multi-core nanoparticles, so-called nanoflowers or colloidal nanoclusters, and mesocrystal systems with properties that are strongly influenced by interparticle interactions [12–15]. Exposing iron oxide nanoparticle dispersions to a magnetic field leads to the formation of one-dimensional (1D) assemblies with unique magnetic properties [16].

Previous studies show that the orientation and amplitude of the assembly field play a decisive role in the formation of magnetic nanoparticle assemblies. Different 1D arrays of magnetic nanoparticle assemblies, such as rods [17], chains [18], needles [19], and helices [20], can be formed in the presence of magnetic fields parallel to the assembly surface, while hexagonal arrays of pillars [20,21] and labyrinthine patterns [22] can be obtained in a perpendicular magnetic field. Additionally, 1D filaments and helices, as well as C-shaped assemblies, can be achieved by adjusting the direction of the magnetic field with respect to the assembly surface [23]. Contrary to studies focusing on the orientation of the magnetic field, detailed studies of the influence of the magnetic field strength, especially in the low magnetic field range, are few. To the best of our knowledge, assembly fields are in the range of 10–150 mT [9,19,20,23–29] and larger than 200 mT [30–33]. The magnetic interactions, i.e., dipole-dipole interactions, and the alignment of the magnetic easy axes strongly depend on the strength of the assembly field [20,34]. Recently, a colossal anisotropy of the dynamic magnetic susceptibility has been reported in 1D needles assembled on Si wafers, which is ascribed to a synergistic coupling between a net anisotropy field from a partial easy axis alignment and the dipolar interaction field [19]. These interactions can result in complex magnetic behaviors of assemblies in the low-field range, requiring further clarification. More importantly, the use of a low magnetic field simplifies device design.

Additionally, spin-glass behaviors related to magnetic interactions have also been investigated in low-dimensional systems. Non-interacting magnetic nanoparticles are superparamagnetic

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at high temperatures, while interparticle interactions for dense nanoparticle systems order the nanoparticle magnetic moments below a critical temperature [35]. Spin-glass characteristics from dipole-dipole interactions between the magnetic nanoparticles, such as long relaxation times, magnetic aging, and memory effects, have been reported for dispersions and 2D systems [36–41]. Furthermore, dipolar interactions can lead to long-range ordering of the nanoparticle magnetic moments [42,43].

In this study, by varying the assembly field (0/1/3/5/30/50 mT), we systemically studied the magnetic properties of low-dimensional assemblies of iron oxide nanocubes at a liquid-air interface, including the magnetic anisotropy of the static and dynamic magnetic responses. Results show that aligned filaments are formed when the assembly field is ≥ 3 mT and duration $t > 14$ min. The interplay between dipolar interactions and the alignment of the nanocube magnetic easy axes are strongly affected by the amplitude of the assembly field. Particularly, spin-glass characteristics are observed in the low-field range. This work reports the assembly field required for low-dimensional assemblies and demonstrates that the spin-glass behavior can be switched on and off, varying the strength of the assembly field. Our work contributes to a comprehensive understanding of magnetic interactions of assemblies and provides a strategy for designing multifunctional assemblies in a weak magnetic field range.

EXPERIMENTAL SECTION

The combination study of liquid and particles refers to the field of nanosynthesis and application, e.g., the liquid phase method [44–46]. Here, oleate-capped iron oxide nanocubes with an edge-length of $l = 13.6$ nm (C136) were synthesized using a thermal decomposition method and their core-shell structure of $\text{Fe}_{1-x}\text{O}|\text{Fe}_{3-\delta}\text{O}_4$ with 5 wt% Fe_{1-x}O had been reported [47]. A nanocube dispersion with a concentration of 7 mg mL^{-1} was prepared by adding cyclohexane and oleic acid. Oriented assemblies were prepared by drop-casting monodisperse oleic acid-capped nanocubes at the air interface of diethylene-glycol (DEG, Aldrich, 99%) in the presence of a magnetic field. A schematic process of the DEG-air assembly under a magnetic field is shown in Fig. 1a1–a3). Each experiment had a Teflon well (diameter ~ 2 cm; height ~ 1 cm) placed between the poles of a magnet. A Helmholtz coil with a diameter of 225 mm was used to generate magnetic fields in the range of 0–5 mT, whereas larger magnetic fields were applied with a BRUKER BE-10 electromagnet. DEG of 400 μL was added to the well and a Si substrate ($4 \times 4 \text{ mm}^2$) was positioned at the bottom of the well, followed by adding 8 μL of nanocube dispersion at the DEG-air interface. The Teflon well was immediately covered with a glass slide and a constant magnetic field was applied in the plane of the DEG-air interface (Fig. 1a1). A series of assemblies at the DEG-air interface was prepared by applying magnetic fields of different strengths and duration and directly monitored using a light microscope equipped with a digital camera. The free-standing assemblies obtained are transferable to various substrates. Here, the DEG was slowly removed from the bottom of the well with a syringe until the assemblies touched down on the Si substrate (Fig. 1a2). The remaining DEG evaporated in a desiccator under reduced pressure to obtain the assemblies on the Si substrate and the direction of the oriented arrays was along the assembly field direction H_{ass} as illustrated in Fig. 1a3.

An Olympus BX60 upright compound microscope with an

OMAX-A3580U3 digital camera was used to record optical microscope images and videos. The orientational distribution of the assemblies was evaluated using the local gradient orientation method in the directionality routine of Fiji-Image [48]. A normal distribution function was used to fit the histograms and the mean orientation angle, full width at half maximum (FWHM), and average filament width were estimated. Furthermore, the assemblies were imaged using a Zeiss-LEO 1550 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Atomic force microscopy (AFM) images were collected using a Bruker MultiMode 8-HR atomic force microscope to determine the dimensions of the iron oxide nanocube assemblies. To observe the arrangement of iron oxide nanocubes inside assemblies, sliced cross-section samples were prepared using an FEI Scios DualBeam FIB-SEM. The morphologies of iron oxide nanocube assemblies were further investigated using a JEOL transmission electron microscope (TEM) F200 operating at a 200 kV accelerating voltage. The angle-dependent magnetization measurements were performed using a LakeShore 7404 VSM equipped with a sample rotation stage. Quasi-static (DC) and dynamic (AC) magnetization measurements were performed in a quantum design MPMS-XL superconducting quantum interference device magnetometer equipped with the ultra-low-field option.

RESULTS AND DISCUSSION

Iron oxide nanocubes assemble at the DEG-air interface in the presence of an external magnetic field. The fabrication process is schematically shown in Fig. 1a. Optical microscope images of the assembled nanocubes under various assembly fields (0–50 mT) were recorded at the DEG-air interface (Fig. 1b). The assemblies evolve from an isotropic ring-shaped porous network in the absence of a field toward an oriented array. Remarkably, the alignment is visible at a low field of 3 mT, where the particles begin to assemble in long intertwined filaments. Fig. 1c, d show the data of the orientational analysis of the images and the image of the 50-mT assemblies, respectively. The data are summarized as orientation histograms and fitted using a normal distribution. An increase in the assembly field increases the alignment of the filaments along the assembly field direction H_{ass} . Further, the distribution of orientations becomes narrower (smaller FWHM, see Fig. 1c). The onset field 3 mT for the alignment is lower than that in earlier reports involving nanocubes with similar sizes on silicon substrates (65 mT) [19] and at the DEG-air interface (17 mT) [20]. At a high assembly field, the DEG-air interface adjusts the assembly morphology to reduce the magnetostatic self-energy of the assembly, yielding low-dimensional curved structures as opposed to 1D needle-shaped structures in the assembly on Si substrates. These results suggest that the interactions of the iron oxide nanocubes with the Si substrate are not negligible due to the less freedom to rotate [49]; the duration of the applied field (t) during solvent evaporation can be relevant. Previous investigations indicate that the structural evolution, ordering, and positioning of assemblies are controlled by t [24,27]. Applying a field of 5 mT results in an isotropic network at $t = 0$ to 12 min; however, for longer durations, the alignment is as shown in Fig. S1a. Even larger magnetic fields cannot induce the alignment at $t = 12$ min (Fig. S1b). Two real-time videos for 0/1 mT assemblies were recorded to investigate the evolution of the assembly process and video clips with a time range of 13–15 min are correspondingly supplemented as Videos

Figure 1 Oriented assembly of nanocubes under an assembly magnetic field. (a) Schematic illustration of the fabrication of assemblies at the DEG-air interface and transfer onto Si substrates. (b) Optical microscope images showing the length and shape of 0/1/3/5/30/50 mT assemblies at the DEG-air interface. (c) Distribution of the orientations of the filaments (top) and data of the Gaussian fits (bottom). (d) Example of the distribution of orientations of the sample prepared with an assembly field of 50 mT. The arrow represents the direction of the assembly field and the scale bars are 20 μm .

SV1 and SV2. Results show that the nanocubes assemble into straight arrays at the DEG-air interface when t is ~ 14 min. As t increases, these assemblies gradually turn into curved filaments. After $t \sim 18$ min, no changes are observed on assemblies. These results demonstrate that the evaporation rate of cyclohexane and the magnetic field conjointly are responsible for the formation of aligned arrays. Hereafter, assemblies fabricated at $t = 25$ min with different strengths of the assembly field are discussed.

The average filament width was obtained using the Gaussian curve fitting from the histograms. Fig. 2a shows that the average filament width reduced rapidly when the applied field changed from 0 to 3 mT, while it decreased slowly as the applied field

further increased. To characterize the mesoscale structure of assemblies, SEM, AFM, and TEM of 5-mT assemblies are shown in Fig. 2b–e. Upon completing the transfer from DEG to the Si substrate, the structure of the oriented assemblies remains the same (Fig. S2 and Fig. 2c). The SEM image in Fig. 2b indicates a disordered arrangement of iron oxide nanocubes on the top surface which was further verified using the variation of the AFM height profile recorded along the length of the nanorod (Fig. 2d). Fig. 2e shows a TEM image of the cross-section with maze-like patterns with one nanocube having an edge length of 13.6 nm presented in the left inset. The image indicates that filaments are composed of locally disordered nanocubes, as

Figure 2 Characterizations of oriented assemblies. (a) Assembly field dependence of average filament width. (b) SEM image, (c) AFM topography image, (d) AFM height trace along the blue line in the inset, and (e) TEM image of the cross-section of 5-mT assemblies. The left and right insets of (e) show the TEM image of an iron oxide nanocube and the fast Fourier transform pattern of the cross-section, respectively. Scale bars (red): 100 nm.

evidenced by the halo in the fast Fourier transform image (see right inset). Similarly, disordered mesoscale structures of 0/50-mT assemblies are shown in Figs S3 and S4. Remarkably, with increasing assembly field, the thickness of assemblies increases (Fig. S4), consistent with the reduction in the average filament width. These observations indicate that the amorphous aggregation of nanocrystals is determined by the strength of the assembly field, where the morphologies and magnetic interactions of assemblies are tuned. Contrary to the ordered structures, i.e., 2D mesocrystals with a simple cubic lattice (0 mT) [29] and 1D needles with a body-centered tetragonal structure (65 mT) [19], this amorphous structure results from the absence of excess oleic acid in dispersions [20].

Fig. 3 shows the DC-magnetic properties of the assemblies transferred to silicon substrates. The low-field magnetization curves of samples and the measuring field parallel to the assembly field H_{ass} , are shown in Fig. 3a, whereas Fig. 3b shows the normalized magnetization values M/M_s of the samples as a function of the angle between the measuring and assembly fields. The details of normalized method are illustrated in Fig. S5. The 50-mT sample measured both parallel and perpendicular to the assembly field exhibits significant anisotropy of the magnetization at low fields. This is consistent with previous results of needle-shaped arrays [19]. For the measuring field parallel to the direction of the assembly field H_{ass} , with increasing strength of the assembly field, the magnetization hysteresis (M - H) curves display an increasing magnetization and a more distinct non-linear magnetic response, proving a significant enhancement of the anisotropy.

Fig. 3b shows the angle-dependent magnetization curves of 0/1/3/5/30/50-mT assemblies at room temperature for a measuring field of 5 mT. No angular dependence is exhibited by 0-mT assemblies (straight line), representing an isotropic magnetic response. However, other assemblies exhibit a sinusoidal angular dependence. To quantify the anisotropy of the DC-magnetic response, we introduce the static anisotropy factor A_{DC} using the ratio of parallel to perpendicular magnetization, i.e., $A_{\text{DC}} = M_{\parallel}/M_{\perp}$, where $M_{\parallel}$ and $M_{\perp}$ are the maximum and minimum values

of the angular-dependent magnetization, respectively, indicated by arrows in Fig. 3b. The assembly field-dependent behaviors of A_{DC} for the 0/1/3/5/30/50-mT assemblies are shown in the inset of Fig. 3b. A_{DC} rapidly increases from 1 to ~ 1.5 when the assembly field is increased to 5 mT, while a gradual but weak increase occurs with a further increase of the assembly field. A static anisotropy factor $A_{\text{DC}} \sim 2.0$ is obtained for an assembly field of 50 mT. Essentially, applying small assembly fields of 1/3/5 mT is sufficient to achieve a considerable degree of magnetic anisotropy, revealing that the nanocubes are highly sensitive to the assembly field applied over the DEG-air interface.

AC magnetization measurements were performed on the 0/3/5/50-mT assemblies in a temperature range of 50–300 K using AC field frequencies of 0.17–510 Hz, as shown in Fig. S6. In all cases, the amplitude of the AC magnetic field was 0.4 mT and it was parallel toward the assembly field H_{ass} . The in-phase (M') and out-of-phase (M'') components of the AC magnetization recorded with an assembly field of 50 mT are shown in Fig. 4a. The M' and M'' versus temperature curves of the 0/5/50-mT assemblies at AC field frequency $f = 0.17$ Hz are compared in Fig. 4b. Results show that the M' and M'' versus temperature curves increase significantly in magnitude as the assembly field increases from 0 to 50 mT. The AC magnetization for 50-mT assemblies with the measuring field perpendicular to the H_{ass} was also measured, as shown in Fig. S7. To quantify the anisotropy of the AC magnetization, the temperature-dependent anisotropy factor A_{AC} was defined as the ratio of parallel to perpendicular in-phase magnetization components. The calculated A_{AC} versus temperature curve for the 50-mT assembly is shown in Fig. 4c, with the peak value of $A_{\text{AC}} \sim 3$. We compared this result with that obtained for 1D C136 needles in [19], where a maximum anisotropy factor as large as 80 was obtained. With the same M' ($\parallel H_{\text{ass}}$) magnitude for needles and filaments, the large difference in anisotropy factor is caused by the larger M' ($\perp H_{\text{ass}}$) of 50-mT assemblies compared with that of needles.

The influence of the assembly field on the relaxation properties of assemblies was investigated by analyzing the peak temperature T_p of the in-phase component of the AC magnetization

Figure 3 Low-field DC-magnetic properties of iron oxide nanocubes assembled in various magnetic fields. (a) Low-field magnetization curves of 0/1/3/5/30/50-mT assemblies with the measuring field parallel to the assembly field direction H_{ass} . The dotted line represents the magnetization obtained with the measuring field perpendicular to H_{ass} . (b) Angle-dependent magnetization of 0/1/3/5/30/50-mT assemblies with a measuring magnetic field of 5 mT. Inset shows the assembly field dependence of the static anisotropy factor A_{DC} .

as a function of AC field frequency f . Previous studies show that the critical slowing down law, $\tau = 2\pi f = \tau_0(T_p/T_g - 1)^{-z\nu}$, can be used to show critical slowing down of the relaxation time (τ) as the spin-glass transition temperature (T_g) is approached, where τ_0 and $z\nu$ are a microscopic timescale related to the relaxation of the individual particle moments and the dynamic critical exponent, respectively. Fig. 4d shows $\ln(\tau)$ versus T_p for the 0/3/5/50-mT assemblies together with fits to the critical slowing down law. Frozen ferrofluids can exhibit spin-glass behaviors when the microscopic relaxation time τ_0 ranges from 10^{-9} – 10^{-8} s [36,37]. Only the results for the 3/5-mT assemblies agree with expectations for a spin-glass system, yielding the fitting parameters $\tau_0 = 1.6 \times 10^{-9}$ s, $z\nu = 12$, $T_g = 175$ K and $\tau_0 = 1.0 \times 10^{-8}$ s, $z\nu = 6.8$, $T_g = 202$ K, respectively, while for the other assemblies, low values of τ_0 are obtained. Thus, these results prove that the spin-glass behavior occurs in assemblies formed using a narrow range of small assembly fields.

To better understand the evolution of the magnetic anisotropy

and the appearance of spin-glass behavior with increasing assembly fields, schematic drawings of C136 nanocube assemblies with varying assembly fields are illustrated in Fig. 5. The C136 nanocubes are superparamagnetic at room temperature, in which the magnetic easy axes correspond to different [111] crystallographic directions (schematically plotted by connecting two diagonally opposite corners in Fig. 5a), and the nanocube magnetic moments in the superparamagnetic state fluctuate in different [111] directions. For simplicity, we ignore possible contributions to the magnetic anisotropy from shape anisotropy. From previous investigations [9,30], the magnetic dipole moment of a particle is defined by $m = \mu_0 \chi V(H + H_{\text{dip}})$, where μ_0 , χ , V , H and H_{dip} denote magnetic permeability of free space, superparamagnetic susceptibility, nanoparticle volume, assembly magnetic field, and dipolar interaction field, respectively. The magnetic dipole-dipole interaction energy between two particles with aligned dipole moments can be expressed as $\mu = -(m^2/4\pi\mu_0 r^3)(3\cos^2\theta - 1)$, where r is the distance between the particles and θ is the angle between $\vec{r}$ and $\vec{m}$. From Fig. 5a, two nanocubes will have negative interaction energy (attractive force) when $\theta = 0^\circ$ and positive interaction energy (repulsive force) when $\theta = 90^\circ$. Therefore, the degree of aligned assemblies and average filament width, to some extent, provides a blueprint of the distribution of dipolar interactions, depending solely on the strength of the assembly field.

The zero-assembly field case reveals a porous network of ring-shaped assemblies formed by dipolar fields due to a few larger nanocubes with blocked magnetic moments at room temperature. These interaction fields, in turn, magnetize smaller (superparamagnetic) nanocubes. Also, the lowest energy state for the zero-assembly field becomes the assembly geometries forming closed magnetic circuits to minimize the magnetostatic self-energy (Fig. 5b, left). In the presence of a relatively weak assembly field (1/3/5 mT), ring-shaped assemblies due to the Zeeman energy and the magnetic torque exerted by the assembly field break up to form more low-dimensional filament structures along the assembly field direction. It also simultaneously introduces the distribution of dipole-dipole interactions, favoring parallel and anti-parallel alignment of the nanocube magnetic moments. Previous simulations show that the dipoles assumed a zigzag configuration unlocked from an assembly field of 16.7 mT [20]. The distribution of magnetic interactions is largely determined by the disorder in the alignment of the nanocube magnetic easy axes, yielding magnetic disorder and frustration (Fig. 5b, middle). For the larger assembly fields (30/50 mT), the aligned filaments indicate a reduction in the width of the distribution of dipole-dipole interactions. The larger fields also rotate the magnetization easy axes of the nanocubes toward the assembly field. A synergistic interplay between dipole interactions and magnetic easy axes establishes the 1D geometry shown in Fig. 5b (right). Electron holography reveals the existence of dipolar ferromagnets in magnetic field-induced 1D structures without crystallinity [33]. These results show that an increase in the assembly field facilitates the anisotropic growth of assemblies by dipolar interactions and the alignment of the nanocube magnetic easy axes along the assembly field direction. Particularly, changing the distribution of interactions between 0–5 mT and 5–50 mT leads to the change of the static anisotropy factor A_{DC} shown in the inset of Fig. 3b.

Magnetic systems should have two characteristics, namely magnetic disorder and frustration, to display spin-glass beha-

Figure 4 (a) In-phase (M') and out-of-phase (M'') components of the AC magnetization *versus* temperature for different AC frequencies and an assembly field of 50 mT. (b) Comparison of M' and M'' at $f = 0.17$ Hz for 0/5/50-mT assemblies with the measuring field parallel to the direction of the assembly field H_{ass} . The solid line represents M' obtained using the measuring field perpendicular to H_{ass} . (c) Anisotropy factor (A_{AC}) *versus* temperature ($f = 0.17$ Hz) for the 50-mT assemblies. (d) $\ln \tau$ *versus* peak-temperature T_p for the 0/3/5/50-mT assemblies. Solid lines correspond to the critical slowing down law (see text for details).

Figure 5 Schematic representation of assemblies formed under different strengths of the assembly field. (a) Magnetic dipole-dipole interactions between nanoparticles induced by an external magnetic field. The blue and red arrows indicate the direction of the nanocube magnetic moment and the direction of the assembly field H_{ass} , respectively. (b) Assembly geometries and direction of nanocube magnetic moments inside assemblies under zero, weak, and strong assembly fields.

viors. A previous study indicates that characteristics of a spin-glass are largely missing in the C136 nanocube platelets, while it exists in the C136 nanocube paste [19]. Further comparison shows that the C136 nanocube platelets have an ordered structure of nanocubes and the C136 nanocube paste is composed of disordered assemblies of C136 nanocubes. Disordered assemblies with a disordered alignment of nanocube easy axes lead to magnetic disorder and frustration, responsible for the spin-glass behavior of C136 nanocube paste. In this study, the interplay between dipole-dipole interactions and disordered alignment of the magnetic easy axes in the presence of a small assembly field (3/5 mT) results in magnetic disorder and frustration (Fig. 5b, middle). However, the alignment of the magnetic easy axes

under a larger assembly field (30/50 mT) forms ordered magnetic interactions (Fig. 5b, right). Theoretically, the lower critical dimension for a low-temperature spin-glass phase is somewhere in the range of 2–3 [50], implying that no phase transition is allowed at a finite temperature below this dimension. Thus, spin-glass characteristics can occur in 3D porous networks of 3/5-mT assemblies and disappear for the 1D filaments of 30/50-mT assemblies. Our work reveals that the assemblies associated with magnetic interactions are tuned using the strength of the assembly field.

CONCLUSIONS

We have systemically studied the properties of the magnetic

field-induced iron oxide nanocube assemblies at the DEG-air interface. Results show that the evaporation rate of cyclohexane and the amplitude of the assembly field determine the geometry of the assemblies. Furthermore, two critical parameters are responsible for the aligned filaments, namely, the onset field ≥ 3 mT and the duration $t > 14$ min. The interplay between dipolar interactions and the magnetic easy axes of nanocubes is tuned using the strength of the assembly field. The ring-shaped assemblies observed for zero-assembly field are gradually transformed by increasing the assembly field from 0 to 50 mT, first to a disordered network intertwined filament-like assemblies and then to 1D assembly filaments with enhanced static and dynamic anisotropic factors. Moreover, the interplay between dipolar interactions and magnetic easy axes in the presence of a relatively weak assembly field causes magnetic disorder and frustration, resulting in spin-glass characteristics. Additionally, the spin-glass characteristics can be induced by weak assembly fields, which are masked in the presence of a large assembly field.

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Supplementary information Supporting data are available in the online version of the paper.

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低场诱导液-气界面纳米颗粒组装体自旋玻璃行为和可控各向异性

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摘要 利用纳米尺度结构单元堆积成具有丰富物理性能的一维(1D)组装体, 是材料设计的研究前沿。然而, 弱磁场诱导1D阵列的制备及其磁性能机制的揭示仍然具有挑战性。本文采用强度不同的组装场(0/1/3/5/30/50 mT), 在二甘醇-空气界面上制备了由无序四氧化三铁纳米立方体组成的低维组装体。随着组装场从0增长到50 mT, 环形组装体先变为细长多孔网状, 再逐步变为细丝阵列, 其中细丝阵列的合成条件为组装场 ≥ 3 mT且施加组装场时间 $t > 14$ min。通过调控组装场强度可得到自旋玻璃特性和静(动)各向异性 $\sim 2(3)$ 。在弱组装场下磁偶极和无序排列易磁化轴之间相互作用导致自旋玻璃特性, 进一步增大组装场将加强磁偶极作用和易磁化轴排列, 导致自旋玻璃特性消失和强各向异性。本研究不仅提出了一种制备自旋玻璃和可控各向异性组装体的策略, 还为理解低维组装磁相互作用提供了新思路。