Field-Directed Self-Assembly with Locking Nanoparticles

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ABSTRACT: A reversible locking mechanism is established for the generation of anisotropic nanostructures by a magnetic field pulse in liquid matrices via the balancing thermal energy, short-range attractive and long-range repulsive forces, and dipole–dipole interactions using a specially tailored polymer shell of nanoparticles. The locking mechanism is used to precisely regulate the dimensions of self-assembled magnetic nanoparticle chains and to generate and disintegrate three-dimensional (3D) nanostructured materials in solvents and polymers.

KEYWORDS: Nanoparticles, nanostructures, self-assembly

Self-assembly is an efficient and scalable method for the fabrication of complex nanostructures from small building blocks such as nanoparticles. This approach has evolved toward the directed self-assembly of specially designed building blocks to generate functional materials by using selective molecular interactions between particulates, constraints at interfaces, template methods, and external fields. These materials possess unique plasmonic, photonic, magnetic, spin memory, and electroconductive properties, to name a few. Here, we introduce a locking mechanism to control the generation of anisotropic nanostructures in liquid matrices by balancing Brownian motion, and short-range attractive and long-range repulsive forces, due to the specially tailored polymer brush shell of nanoparticles, as well as the forces acting on the particles in an external magnetic field. A reversible locking mechanism is used to precisely regulate the dimensions of self-assembled magnetic nanoparticle chains and to generate 3D nanostructured materials in solvents and polymers.

The field-directed assembly of colloids in suspensions implies the use of field-induced polarization and strong dipole–dipole interactions to guide the particle assembly into the desired configurations. In well-known examples of electro- and magnetorheological fluids, the field-induced particle interactions overcome Brownian motion and the particles form dipolar chains that coalesce with time. Particle functionalization and the use of different shapes of particles in combination with external fields is a promising methodology for the fabrication of complex anisotropic nanostructures.

Field-directed particle assembly has several limitations related to the generation of complex nanostructures. First, the structures change dynamically as long as an external field is on. Hence, simultaneous control over the length and diameter of 1D chains assembled from nanoparticles is a challenging problem. Second, the structures are generated in accordance with the field direction (along the field or in the orthogonal direction). A change of the field direction will result in a realignment of the structures. Third, the structures may be destroyed if the field is removed. Traditionally, particles are stabilized electrostatically and sterically using surfactants and polymers to yield stable colloidal suspensions. Thus, when the external field is turned off, the assembled structures are disintegrated by thermal motion (when the particles are not glued together).

These constraints lead to the applications of the field-directed assembly, which are limited to the cases of switchable and reconfigurable assemblies, when turning an external field on and off is used to temporarily alter the structure and rheology of the materials and fluids, or for the synthesis of 2D- and 3D-colloidal crystals (which requires prolonged exposure to permanent or oscillating fields). More complex anisotropic structures, indeed, can be attained by using field-directed self-assembly of nonspherical particles and at

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when the spatial constraints change the mechanism of particle assembly. There are also methods reported for the scalable field-directed formation of stable (after removal of a magnetic field) chains of magnetic nanoparticles based on the permanent locking of the structures via covalent and non-covalent bonding. However, these methods have limitations for the fabrication of bulk materials and scaling up. There are as well limitations in control over the nanowire length and thickness, energy of interactions, 3D alignment, and reversibility of self-assembly.

Here, we introduce a method for field-directed self-assembly using specially designed spherical core–shell magnetic particles with locking properties of the polymeric shell. Specifically, we synthesized responsive nanoparticles that are capable of reorganization in an external magnetic field. The magnetic field turns on interactions between the particles. The interaction remains unchanged even after the removal of the external magnetic field due to the specially tailored polymer shell of the nanoparticles. This mechanism is termed here the “locking mechanism.” The “locking particles” can be unlocked by applying external stimuli, such as changes in temperature or in pH. We also demonstrated that a mixture of two populations of nanoparticles with different surface functionalizations that provide control over intermolecular forces can be used to regulate the length of the self-assembled 1D chains. The chains can be used as the second generation building blocks for the field-assisted fabrication of 3D-nanostructured materials.

In the examples presented here, 30 and 100 nm particles, made of γ-iron oxide, were enveloped by a thin silica shell and decorated by tethered polymer chains of poly(2-vinylpyridine-b-ethylene oxide) (P2VP-b-PEO) block copolymer, which provided colloidal stability to the particles and imbued them with the mechanism of reversible locking. The spherical magnetic nanoparticles encapsulated into a silica shell with a mean diameter of 50 and 100 nm (core plus shell) were synthesized using two different methods described in refs 27 and 28, respectively. Although similar results were obtained for both samples of the particles, in this article we report the results obtained for particles with the 30 nm core. For synthesis of the locking particles, the silica shell was functionalized with (3-bromopropyl)trimethoxysilane, and then P2VP-b-PEO (Mn = 3000 g/mol for P2VP and Mε = 9000 g/mol for PEO) was grafted via a quaternization reaction in nitromethane at 60 °C. The thickness of the grafted polymer shell was 7 ± 1.5 nm (as measured using scanning electron microscopy (SEM) and atomic force microscopy (AFM)). Details regarding particle synthesis, functionalization, and characterization are available in Supporting Information.

The water-soluble nonionic PEO layer constitutes the outer shell of the nanoparticle. The PEO shell has a low interfacial energy in an aqueous environment. The PEO shell contributes a steric repulsive force when interacting with other particles. P2VP chains are not soluble in water at pH > 4 due to a hydrophobic backbone. P2VP macromolecules, however, can be protonated and dissolved in an acidic aqueous solution. In general, P2VP demonstrates the properties of a weak polyelectrolyte. The polymer is soluble at pH < 4 due to the protonated charged pyridine nitrogen when electrostatic repulsion overcomes the short-range hydrophobic attraction in the backbone of the polymer chain. Conformation of the P2VP chain is sensitive to the pH and ionic strength of aqueous solutions.

In an external magnetic field, the kinetically stable particle suspension (Figure 1a) forms discontinuous strings (Figure 1b), which was monitored in situ in suspensions using dark field optical microscopy. The particles are locked in the strings because the field-induced forces bring particles into close contact when the locking mechanism comes into effect. This locking mechanism is not directly related to magnetism, but is caused by the interaction between the specially designed polymeric shells of the particles. When the magnetic field was removed, the strings remained intact (Figure 1c, Supporting Information, Video 1) due to the particle locking. This behavior of the particle suspension was compared with the reference particles that did not possess any locking shell. The particles with grafted PEO chains were used in the reference experiment. PEO-decorated particles were prepared by grafting 3-amino propyl terminated PEO (Mε = 1500 g/mol) to the surface of the core–shell magnetic particles, which were functionalized with 3-glycidoxypropyl trimethoxysilane. The PEO-decorated particles formed stable colloids due to steric repulsion between the PEO grafted layers. The strings, which were formed when the magnetic field was applied to the reference sample, were destroyed by thermal motion and the particles returned to the original state of the stable colloidal suspension after removal of the magnetic field (Supporting Information, Video 2).

The mechanism of locking is demonstrated first using an example of the interaction of a plane substrate (Si-wafer) and an AFM tip. The surfaces of both materials were functionalized by grafting a P2VP-b-PEO copolymer with molecular weights of 3 and 9 kg/mol for the P2VP and PEO blocks, respectively; the architecture of the grafted layer is schematically shown in Figure 2a,b. The hydrophobic P2VP surface is screened by the swollen hydrophilic PEO brush (Figure 2b). In the approach mode, when the AFM tip approaches the Si-wafer, the brushes exert a repulsive force at pH 5.5 (Figure 2d and e). A further movement of the tip toward the wafer brings the two surfaces into contact when they are locked due to hydrophobic interactions (Figure 2g and h). The locking effect manifests itself as a nonzero pull-off force in the withdrawal mode.
Thus, in an aqueous environment at $5.5 > \text{pH} > 3.5$ two solid materials decorated with the grafted copolymer can be locked to each other due to hydrophobic interactions between the P2VP blocks if the external force overcomes the steric repulsion (Figure 2d) of the PEO blocks and the tip-Si-wafer interaction is governed by hydrophobic forces (Figure 2g). Thus, we observe the locking effect in the range $5.5 > \text{pH} > 3.5$.

At pH < 3, the P2VP chains are charged and swollen. In acidic solutions, the two surfaces are repulsive due to the combination of steric and electrostatic repulsions (Figure 2c and f). There is no locking effect in this pH range.

The diagram in Figure 2i is a summary of the pH-dependent balance between the energy ($E_A$) needed to bring the polymer-decorated AFM tip and Si-wafer into contact and the energy ($E_R$) needed to retract the AFM tip once it is in contact with the Si-wafer. The $E_A$ and $E_R$ values were obtained by the integration of the repulsive and attractive parts of the force-distance curves (Figure 2c, d, f, and g), respectively. This diagram helps to predict and explain the behavior of colloids decorated with the P2VP-b-PEO grafted copolymer. In the range of pH values between pH 3.5 and pH 5.5, $E_A$ is high enough to stabilize colloids, whereas $E_R$ is sufficient to lock particles via hydrophobic interactions between the P2VP blocks as soon as the particles are in intimate contact. (The theoretical estimates for $E_A$ and $E_R$ are presented in the Supporting Information.) Thus, if the external force overcomes the repulsions in this pH range, the colloids will be locked into aggregates.

The graphs in Figure 2j show the dynamic light scattering hydrodynamic radii of silica particles (nonmagnetic particles) that are decorated with the P2VP-b-PEO copolymer in comparison with the reference colloidal particles: the bare silica particles and the silica particles decorated with grafted PEO and P2VP polymers. The dynamic light scattering (DLS) data were used to distinguish between colloidal dispersions of nonaggregated particles and aggregated particles. No aggregation was observed for the silica and PEO-coated particles. The P2VP-coated particles aggregate strongly when P2VP turns into the hydrophobic state at pH > 5.5. For the P2VP-b-PEO decorated particles, aggregation is detected at pH > 5.5. Thermal energy overcomes repulsion at pH > 5.5 (Figure 2j).

Figure 2. Conditions for the locking effect. (a and b) Schematics of a P2VP-b-PEO brush at ionized (a) and nonionized states (b). (c–h) The surfaces of a brush-coated Si-wafer and an AFM tip (simplified geometry of a spherical particle) are repulsive at pH 2 (c) and 5.5 (d) in the approaching mode due to steric plus electrostatic interactions (e) and repulsive at pH 2 (f) and attractive at pH 5.5 (g) in the withdrawal mode due to the hydrophobic locking effect (h). (i) Dependences of the energy of approaching, $E_A$ (black squares), and retraction, $E_R$ (red circles), on pH exhibit three regions of colloidal stability of the brush-decorated nanoparticles: stable colloids, kinetically stable colloids (conditions for the locking effect), and unstable colloids. (j) The above data are in accord with the results of light scattering measurements for the P2VP-b-PEO-decorated particles vs the reference silica, PEO- and P2VP-coated particles.
and the colloids aggregate. Thus, colloidal dispersions of the P2VP-b-PEO decorated particles are stable in a broad pH range below pH 5.5 without an external magnetic field, and we could expect the locking effect at pH < 5.5 according to the mechanism depicted in Figure 2.

This concept of locking has been applied to suspensions of magnetic particles when an external magnetic field was used to activate the locking mechanism. The dispersion was kinetically stable at room temperature at pH < 5.5 (Figure 2i). In the magnetic field, the dipole−dipole interaction overcame the steric repulsion, and the generated strings of magnetic particles were locked and stabilized by hydrophobic forces (Figure 1b,c). However, changes in pH from 5 to 2 led to disassembly of the strings and formation of a stable particle suspension (Figure 1d) due to ionization of P2VP chains and strong electrostatic repulsion between the particles. Consequently, within the pH range of 5.5 > pH > 3.5 when $E_A$ is high enough to stabilize the colloids and $E_R$ is sufficient to lock the particles, the external magnetic field was used to overcome the $E_A$ barrier and reversibly lock the particles. A decrease in pH below pH 5.5 results in unlocking the particles due to strong electrostatic and steric repulsions.

It is evident that different kinds of particle−particle interactions could be explored for the locking mechanism. In another example, we used the P2VP-b-PEO decorated nanoparticles that were further modified with 2–4 nm Prussian Blue (PB) clusters as described in the Supporting Information. The PB clusters were deposited and adhered to the P2VP chains in the particle shell. The PB clusters interact strongly with P2VP blocks so that the PB clusters can be used to lock the particles aggregates as soon as they are brought in close contact by the external magnetic field. In other words, we replaced the hydrophobic locking mechanism in aqueous suspensions by locking due to the P2VP-PB interactions between particles in polymer melts. This replacement enables the locking mechanism in a nonaqueous environment, for example, in polymer melts. In our experiments, the PB clusters were used to lock the particle strings via P2VP-PB-P2VP bridging in PEO polymer melts of various molecular weights in the presence of a magnetic field. For a higher molecular weight PEO, that is, PEO 1500 g/mol, the sample was locked at 60 °C (above the melting point of PEO) to enable free movement of the particles. The obtained strings were stable up to 75 °C in PEO 200 g/mol and up to 120 °C in PEO 1500 g/mol after the magnetic field was removed. At higher temperatures we observed a fragmentation of the strings with complete disassembly and aggregation at 160 °C in PEO 1500 g/mol as shown in the in situ (in melt) experiments using dark field optical microscopy (Figure 3).

Thus, the locking mechanism can be used to preserve anisotropic nanostructures in solutions and polymeric matrices via exposure of the material to a pulse of a magnetic field. That brings a substantial technical advantage in terms of energy saving for the fabrication of anisotropic composites. An anisotropic composite with common magnetic particles could be prepared by hardening the composite in a magnetic field until the solid or cross-linked polymer stabilizes the assembled particles. For structures with the locking mechanism, the magnetic field could be switched off as soon as the structures are formed. The locking mechanism will preserve the structures while the process of hardening is conducted.

Physical properties, including conductivity and optical and mechanical properties of composite nanostructured materials, depend on the dimensions of nanostructures. The locking effect brings a new opportunity for control over the dimensions of nanostructures, as discussed below.

The length of the particle chains depends on the balance of thermal energy and the energy of dipole–dipole interactions in the magnetic field. In a strong magnetic field, magnetic chains are very long; however, they disintegrate as soon as the field is...
The situation is quite different for the locking particles. As soon as the magnetic field is off, the length of chains is affected by the balance of the energy of the particle repulsion, the energy of locking, the energy of dipole–dipole interactions between the particles in the chain (at the moment when the magnetic field was on), and the strength of the magnetic field (when it was on). The polydispersity of the particles by size manifests itself in the dependence of the chain length on the strength of the magnetic field (see the Supporting Information for a more detailed discussion). If the locking is not activated for some fraction of the nanoparticles (because the balance between the forces is particle size dependent), then the particle chain is broken in that unlocked site after the magnetic field is turned off (Figure 4a–e). Thus, a fraction of “defective particles” (by size and quality of coatings) creates defects in the particle chains (locking is not activated at the given strength of the magnetic field). In locations of those defects, the particle chains are “cut” by thermal energy.

Control over the particle chain length could be attained using specially incorporated defects via a combination of two populations of magnetic nanoparticles. One population of the nanoparticles has a shell with the locking effect, whereas...
The combination of both the locking effect and the control over the particle length offers an additional opportunity to generate 3D nanostructured materials as shown in Figure 4(k)–(o). The mobility of the magnetic chains obviously depends on their length. By optimizing the mobility characteristics through the adjustment of the chain length, we found a regime in which a rotation of the magnetic field could be used to approach an entanglement of the particle chains and the formation of a 3D network. For example, exposure of a suspension of locking nanoparticles to the 18 mT field resulted in the formation of 25 μm long chains (Figure 4k) in which the particles were locked, as concluded from the lack of any sign of chain breakup after removal of the field (Figure 4l). The subsequent exposure of this aligned structure to the magnetic field applied in orthogonal directions led to the formation of a 3D network of the chains (Figure 4m). The 3D network was locked through the same mechanism. Experiments with a change in the magnetic field direction (Figure 4n) and then the reversion of the field (Figure 4o) revealed the recovery of the same network patterns. In particular, the experiments showed that the initially formed network (Figure 4m) deformed elastically by the redirected magnetic field (Figure 4n) and relaxed after the field direction was restored (Figure 4o). The reversible deformation of the field-assembled 3D network was confirmed through a quantitative analysis of the particle strand conformation (see Supporting Information).

In summary, the generated structures demonstrate that a combination of locking and antilocking nanoparticles is a powerful tool to control the anisotropic self-assembly of nanostructures in external fields. Obviously, the particles could be prepared from metals and semiconductor materials. Self-assembly could be attained in magnetic or electric fields (in the latter case in a dielectric environment). The energy of particle–particle interactions in the locked state could be regulated by appropriate selection of the locking mechanism. All of those combinations could bring into existence a number of novel approaches for the development of nanostructured composite materials with advanced optical, conductive, magnetic, and mass transport properties.