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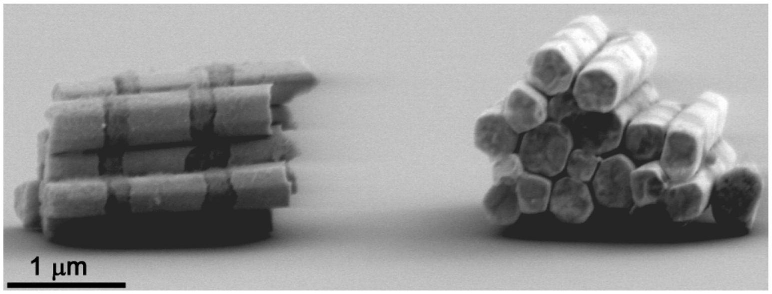

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Three-Dimensional Self-Assembly of Metallic Rods with Submicron Diameters Using Magnetic Interactions

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This paper describes the three-dimensional (3D) self-assembly of metallic rods with submicron diameters into highly stable microstructures using magnetic interactions to guide the assembly process. The rods contained alternating sections of ferromagnetic and diamagnetic materials. The ferromagnetic sections were disks, that is, their thickness (t) was less than their diameter (d), and their dominant (or "easy") axis of magnetization was perpendicular to the long axis of the rods. After these rods were magnetized, they spontaneously assembled into stable "bundles" in the absence of an external field. This work demonstrates that the magnetic profile of individual components can direct and stabilize the formation of ordered, 3D structures by self-assembly.

The application of a magnetic field to a suspension of magnetic particles (microspheres, nanoparticles, and rods) typically produces one-dimensional (1D) chains of particles with their magnetic dipoles aligned head-to-tail, parallel to the magnetic field;[1,2] these assemblies usually require an external magnetic field to remain stable in suspension. Ordered, two-dimensional (2D) lattices of magnetic particles have been demonstrated, but these structures also destabilize when the external magnetic field is removed from the system.[3] There have been no demonstrations of 3D assemblies of microstructures by magnetic interactions. The fabrication of 3D microstructures is difficult, but self-assembly provides a strategy for generating ordered arrays. 3D microstructures generated with capillary interactions between small particles (10 nm to 10 μm) have been useful, in part, because capillary forces extend over a large range of sizes.[4] Ferromagnets also have this characteristic and, therefore, should offer an alternative to 3D self-assembly.

We hypothesized that rod-shaped particles would assemble side-by-side (logs in a raft) if they contained ferromagnetic sections with their easy axis of magnetization perpendicular to the long axis of the rod. Searson and co-workers demonstrated that ferromagnetic sections in metallic rods magnetize perpendicular to the long axis of the rod when their thickness (t) is smaller than their diameter (d).[5] These sections should align head-to-tail, akin to 1D chains, leading to lateral assembly of the rods.

The fabrication of metallic rods by electrodeposition, following techniques developed by Martin[6] and Mallouk,[7] is a convenient method for generating rods with control over the size and separation of the ferromagnetic components. We designed rods to contain two ferromagnetic sections (nickel) separated by diamagnetic sections (gold) (Figure 1a) to increase the stability of the assembly through simultaneous magnetic interactions (Figure 1b). Rods of alternating layers of gold and nickel were deposited in porous alumina filters and released by dissolving the alumina filter in 0.5 M KOH solution.[8] The rods were collected by centrifugation and washed with water.

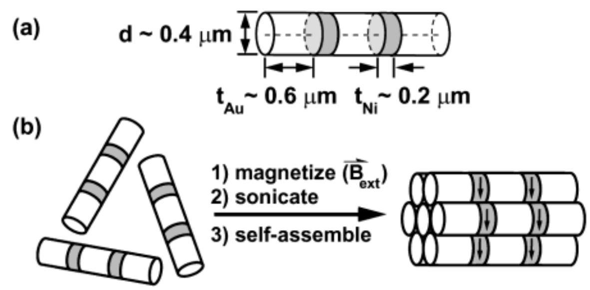

Figure 1. Schematic diagram of (a) a microscopic rod containing alternating sections of gold and nickel where the magnetic sections have an aspect ratio (t/d) of ~0.5; (b) self-assembly of rods (the arrows on the nickel sections indicate the "easy" axis of polarization).

The process of self-assembly comprised three steps. First, the nickel sections of the rods were magnetized using a NdFeB magnet. After the magnet was removed, the rods remained aggregated; this observation suggested that the nickel sections were ferromagnetic. Second, the rods were resuspended by ultrasonication. This process yielded a dense, uniform suspension of rods that clarified within 10−30 s; this observation corresponds to the assembly of the rods.[9] Third, an aliquot of this suspension was deposited and dried onto a silicon wafer for imaging by optical and scanning electron microscopy.

We observed "bundles" of rods scattered over the silicon wafer, with few individual or isolated rods (Figure 2a). The rods in each bundle were oriented side-by-side with their long axes parallel to one another and their ferromagnetic sections aligned (Figure 2b). While we expected to observe the side-by-side assembly of rods, the formation of bundles was unanticipated.

Variation in the number of rods per bundle (10−100) and in the shape of the bundles may result from irregularities in the geometry of the individual rods, which replicate the shape of the pores in the alumina template. The diameters varied by up to 50%, and the cross sections were multifaceted polygons. Despite these irregularities, we rarely observed defects in packing or in alignment of rods; the few defects we observed (<1%) were due to missing rods.

The bundles persisted stably for longer than 2 months without an applied magnetic field. In an effort to break the bundles into individual rods, we dispersed an aliquot of the rods in hexanes by ultrasonication and deposited the rods within 3−5 s on a glass slide. Although this process yielded many individual rods on the surface of the slide, we observed no individual rods when the interval of time between the cessation of sonication and the deposition exceeded 10−15 s.

We tested the hypothesis that the rods must contain ferromagnetic sections with aspect ratios less than 1 ($t < d$) to form ordered, 3D assemblies. When exposed to an applied field and then deposited, rods containing ferromagnetic sections with $t > d$, $t = d$, or lacking ferromagnetic material altogether formed randomly oriented ag-

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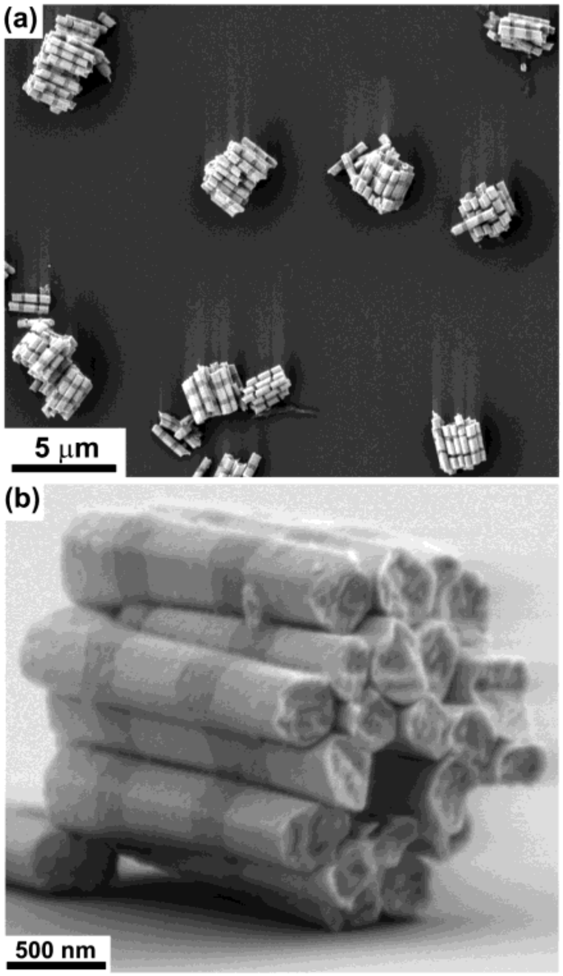

Figure 2. (a) Scanning electron micrograph (SEM) of multiple bundles of rods. The light sections are gold, and the gray sections are nickel. The aspect ratio of the ferromagnetic sections is ∼0.5. (b) SEM of a single bundle demonstrating the alignment of ferromagnetic sections.

gregates. When deposited in the presence of an applied field, however, rods with $t > d$ produced 1D chains, as observed previously.[2] We conclude that only rods containing ferromagnetic sections with $t < d$ assemble into ordered 3D structures using magnetic interactions.

The experimental results suggest that (1) small bundles of rods nucleate homogeneously throughout the suspension within seconds after ending sonication; (2) magnetic forces between rods stabilize the bundles; and (3) the bundles do not interact strongly with each other. These results further suggest that the magnetic dipoles in a bundle are ordered such that the bundle has little or no net magnetic dipole.

We built a magnetic macroscale model of the rods to determine the orientation of magnetic dipoles that corresponds to the most stable configuration (see Supporting Information).[10] The most stable arrangement of the macroscale rods was a close-packed lattice. The dipoles in this structure orient in head-to-tail rings; that is, they form concentric closed loops aligned in the same direction. A simulation of the magnets in this structure, using a finite element method,[11] demonstrated that the bundle had an insignificant net dipole and that the magnetic flux was confined almost entirely within the bundle. This confinement minimizes the coalescence of bundles into larger assemblies, because the magnetic interactions between bundles are weak.

This paper demonstrates the first 3D self-assembly of metallic rods with submicron diameters into stable microstructures. The strategy for assembly used magnetic forces between ferromagnetic rods to organize and stabilize the microstructures. Magnetization of the ferromagnetic disklike sections within individual rods polarized them perpendicular to the physical (long) axis of the rods and promoted lateral interactions that directed the self-assembly of the rods. These results, in combination with our macroscopic model, suggest a principle for designing 3D assemblies of magnetic objects: formation of stable microstructures using magnetic forces requires the magnetic dipoles of individual elements to arrange in a manner that reinforces their interactions with nearest neighbors and minimizes the energy of the system; that is, self-assembly should be designed to allow closed loops of head-to-tail dipoles.

Magnetic and capillary interactions are complementary in 3D self-assembly: magnetic (1) forces act in both air and liquid; and (2) objects do not require specific surface chemistries for interaction. Objects with specific surface chemistries are difficult to fabricate with critical dimensions less than 1 μm.[4] Magnetic self-assembly has broad potential because a wide range of micro- and nanostructures can be fabricated by electrodeposition, CVD, and other methods.

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Supporting Information Available: Experimental details. Macroscopic model and finite-element calculation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Gold and nickel were selected for the sections in the rods primarily for convenience. See Supporting Information for details.
(9) A suspension of unmagnetized rods persists for several minutes (>3).
(10) This model should predict the behavior of the microscopic rods because the extent of magnetic interactions between ferromagnetic objects scales with their size.
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