

## Polyelectrolyte Stabilized Nanowires from Fe<sub>3</sub>O<sub>4</sub> Nanoparticles via Magnetic Field Induced Self-Assembly

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Received June 14, 2005

Revised Manuscript Received December 15, 2005

Magnetic nanoparticles constitute a system of wide research interest encompassing such fascinating aspects as superparamagnetism,<sup>1</sup> dipolar interactions,<sup>2,3</sup> ferrofluids, and rheology.<sup>4,5</sup>

Ordered superlattice structures in all one,<sup>6</sup> two,<sup>7</sup> and three<sup>8,9</sup> dimensions have been obtained from a stable colloid by controlled evaporation, spin coating, Langmuir–Blodgett deposition, and so forth. Such controlled assembly gives rise to varied architectures, generating interesting collective properties.<sup>10,11</sup> Appreciable effects were observed at very small distances where dipole–dipole interactions dominate the collective properties of the organized structures.<sup>9</sup> Capillary forces,<sup>12</sup> confinement effects,<sup>10,13</sup> shape-selective<sup>14</sup> as well as size-selective<sup>15,16</sup> interactions, and template synthesis<sup>17,18</sup> are intensively investigated for the directed self-assembly of nanoparticles. Among these, the template approach appears to be very straightforward and effective.

Polymers can be used as templates. Self-assembled block-copolymer morphologies were used to prepare superlattices of nanoparticles.<sup>19</sup> Single polyelectrolyte molecules were templated with metal nanoparticles; initially, giant DNA molecules<sup>20–22</sup> and later “thin” synthetic polyelectrolyte chains<sup>22,23</sup> were employed to produce one-dimensional (1D) nanowires. Very often, because of mutual electrostatic repulsion of the nanoparticles, deposited particles are separated by large distances where the interaction between particles is substantially decreased.<sup>24</sup> Magnetic forces overcome thermal motion and electrostatic repulsion between the nanoparticles.<sup>25</sup> This approach allows for the very simple fabrication of 1D structures of densely attached nanoparticles in aqueous solution. Reversible formation of 1D structures from paramagnetic particles induced by magnetic field has been used to tune properties of magnetorheological fluids,<sup>26</sup> separate biomaterials, and manipulate microscopic fluid flow.<sup>27</sup> Furst et al.<sup>28</sup> have developed methods for permanent linkage of paramagnetic colloidal particles (0.5 μm in size) under external magnetic field, employing covalent linkage between the specially functionalized polystyrene latex particles filled with magnetite. Recently, a few other groups have reported permanent binding of magnetic nanoparticles with polymers.<sup>29–33</sup> Field induced phase aggregation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles has been experimentally demonstrated elsewhere.<sup>34</sup>

In the present report, we use magnetic field for the fabrication of wire-like structures made by linking Fe<sub>3</sub>O<sub>4</sub> superparamagnetic nanoparticles (SPN) with polyelectrolyte molecules. These wires are structures wherein the SPN particles are linked permanently and they conserve the shape

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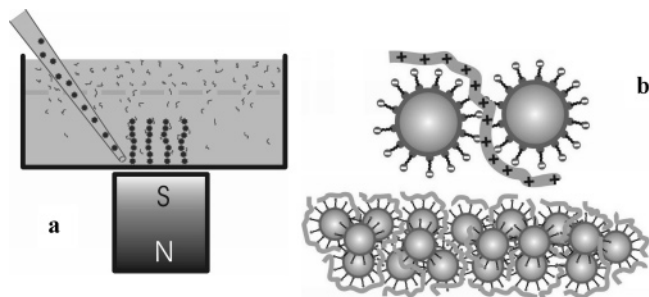
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**Figure 1.** Liquid cell used for the synthesis of magnetite nanowires (a) and schematic representation of the structure of magnetic nanowires stabilized by P2VPq (b).

inspite of thermal motion in the fluid. Further, upon deposition onto solid substrates in the presence of an external magnetic field, they form parallel patterns which remain attached to the substrate with lithography-like stubbornness and, thus, are immune to washings and changes in the direction of the applied magnetic field.

The synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles (see Supporting Information for synthesis and analysis of the particles) with a dominant population of 10–12 nm are obviously monodomain; they show superparamagnetic behavior at room temperature and blocked hysteresis loop in magnetization curves at low temperature, as reported elsewhere.<sup>6,35</sup> We fabricated nanowires from the SPN by using the cell shown in Figure 1a. The plastic cell was mounted on a magnet with a nominal field of 1 T. The original particles are stabilized by citric acid, and their surface is negatively charged in aqueous solutions, as determined by electrophoresis.<sup>35</sup> We used the positively charged polyelectrolyte poly(2-vinyl *N*-methylpyridinium iodide) (P2VPq;  $M_n = 6000$  g/mol) to stabilize the wires via formation of a polyelectrolyte complex. The cell was filled with 5 mL of Millipore water, and 0.1 mL of 0.1 g/L SPN solution was slowly injected with a pipet on the bottom of the cell. To create a slow diffusion flow of the P2VPq to the SPN we separated them by a membrane. The cellulose membrane (0.4  $\mu\text{m}$  pore size) was mounted on the top of the cell so that the membrane was slightly immersed into water. On the top of the membrane we introduced 0.5 mL of 5 g/L P2VPq aqueous solution. The experiment was run overnight. Afterward the aqueous solution was extracted with a pipet, and the nanoparticles concentrated at the bottom were rinsed with water several times to wash off the excess of P2VPq. Then the magnet was removed and the dispersion of the nanowires was used for further investigations. The representative transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of the wire-like structures are shown in Figure 2. In a reference experiment conducted in the absence of magnetic field, we discovered only a randomly distributed array of original nanoparticles.

The length of nanowires formed by 90 (an average value) aligned and densely packed original SPN is in the range of 1.5  $\mu\text{m}$ . The wires can be considered as particle–surfactant–polymer composites. While the citric acid layer resides on the surface rendering a negative charge, the polyelectrolyte P2VPq anchors to those charges via the positively charged

ammonium ion on the chain (schematically shown in Figure 1b). This is also noted from the Fourier transform infrared spectra (Supporting Information, Figure 3) of the composite when compared with that of the neat P2VPq. The X-ray photoelectron spectrum (Supporting Information, Figure 4) also depicts the presence of nitrogen on the multiply washed composite sample, illustrating the binding of the P2VPq onto the particles surface. Additional evidence for the stabilization effect introduced by P2VPq was obtained from Z-potential measurements (Supporting Information, Figure 5). Adsorption of the positively charged P2VPq results in a change of the Z-potential of SPN from negative to positive. According to the thermogravimetric (Supporting Information, Figure 2) analysis the content of the citric acid layer on the initial SPN was 2.7% of the particles weight, while the content of the organic shell on the SPN with P2VPq coating was 6.1%.

Because of magnetic dipole–dipole interactions among the magnetic nanoparticles, it is expected that they form wire-like structures in diluted magnetic liquids.<sup>36</sup> In concentrated magnetic fluids, calculations suggest that strong interaction may lead to macroscopic parallel alignment of dipole moments, yielding a liquid permanent magnet.<sup>37,38</sup> As was shown in the literature,<sup>39</sup> SPN consist of single domains. Each approximately spherical magnetic particle can be considered as a point dipole located at the center of the particle with a given magnetic moment. The configuration that is energetically most favorable is the one that has both dipoles along the same direction and is aligned south to north. The estimated interaction energy of the dipoles at room temperature implies that one should observe coagulation of particles (see Supporting Information). However, in reality, the Brownian motion destroys the perfect alignment needed to minimize the energy, which results in a decrease in the interaction.<sup>39</sup> Applying an external magnetic field can modify interactions between magnetic particles. The energy of interaction of a single magnetic particle and an external field (1 T) for a 15 nm particle of  $\text{Fe}_3\text{O}_4$  corresponds to  $\sim 220$  kT. Therefore, the external field is strong enough to align magnetic moments of the particles along the field, despite thermal motion.<sup>25</sup> This increases the average strength of particle–particle interaction to the maximum value that should be sufficient to give rise to a wire-like structure. The aligned particles linked by the polyelectrolyte complex, however, retain their wire-like shape in the absence of magnetic field because of the formation of low-mobility composites constituting the polyelectrolyte and nanoparticles.<sup>40</sup>

These wires, stabilized by polyelectrolyte complex in the solution, can be cast onto a substrate and dried into patterns. It should be noted that these aligned nanowires constitute an anisotropic system. Magnetization hysteresis on these aligned wires was measured, and it was found that the coercive fields show differences when the magnetic field during the measurement was parallel and perpendicular to the patterns, respectively (see Supporting Information, Figure 7).

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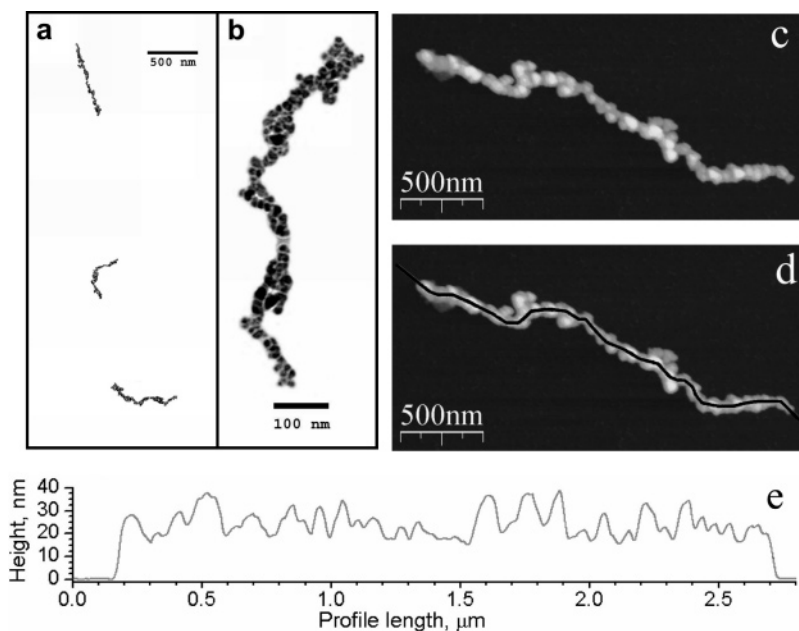
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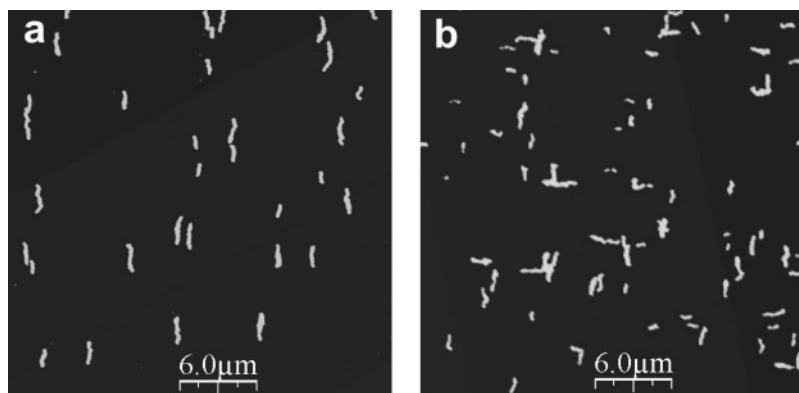
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**Figure 2.** TEM images [bar = 500 nm (a), bar = 100 nm (b)] and  $5 \times 2.5 \mu\text{m}^2$  AFM images of the magnetic wire-like structures stabilized by P2VPq: original (c) and with a line (d) which shows the locus of the cross section (e).



**Figure 3.** Magnetic nanowires aligned in a magnetic field and deposited on the Si wafer (a); the complex structures fabricated from the nanowires (T- and X-shaped) when the second portion of the nanowires was aligned in a magnetic field in the direction perpendicular to case a and deposited on the top of the structures (a).

The magnetic nanowires can be manipulated in an external magnetic field. They can also be used as building blocks for the fabrication of hierarchical two-dimensional (2D) and three-dimensional (3D) structures. We demonstrate this feature with further experimental findings. The nanowires were deposited on the mica substrate in the presence of an external magnetic field. The mica substrate was mounted on the top of the magnet. A drop of the nanowire solution was set on the surface of the substrate for several minutes. Subsequently, the magnet was removed and the sample was rinsed with water. The alignment of the nanowires was visualized with AFM (Figure 3a). The image reveals the alignment of wires in the direction of the magnetic field. Next, we turned the magnet to a perpendicular position and repeated the deposition of a second portion of the nanowires. The AFM image demonstrates the alignment of the nanowires in a direction perpendicular to that obtained in the first deposition experiment. We observe the formation of T-shaped and X-shaped structures (Figure 3b). The nanowires deposited in the first experiment are trapped by the substrate and are no longer free to make any rotational movement in response to the perpendicular field applied. However, the

nanowires deposited in the second step were oriented along the magnetic field created in the perpendicular direction by the magnet positioned in the new direction. This experiment demonstrates the potential capability to fabricate different robust structures akin to lithography, using magnetic wires as building blocks. Magnetic field will allow addressing and manipulation of the nanowires and enable fabrication of various patterns on large surface areas.

**Acknowledgment.** The work at The State University of New York at Buffalo was supported by a Defense University Research Initiative on Nanotechnology Grant through the Air Force Office of Scientific Research. The work at Clarkson University was supported by NSF Grant CTS-0456548. R.S. thanks Graduate Student W. Coulter Foundation Fellowship awarded via Clarkson University and NYSTAR CAMP.

**Supporting Information Available:** Experimental and instrumental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.