Developing Biotemplated Data Storage: Room Temperature Biominalization of L1₀ CoPt Magnetic Nanoparticles

Johanna M. Galloway,* Jennifer E. Talbot, Kevin Critchley, Jim J. Miles, and Jonathan P. Bramble

L₁₀ cobalt platinum can be used to record data at approximately sixfold higher densities than it is possible to on existing hard disks. Currently, fabricating L₁₀ CoPt requires high temperatures (≈ 500 °C) and expensive equipment. One ecological alternative is to exploit biomolecules that template nanomaterials at ambient temperatures. Here, it is demonstrated that a dual affinity peptide (DAP) can be used to biotemplate L₁₀ CoPt onto a surface at room temperature from an aqueous solution. One part of the peptide nucleates and controls the growth of CoPt nanoparticles from solution, and the other part binds to SiO₂. A native silicon oxide surface is functionalized with a high loading of the DAP using microcontact printing. The DAP biotemplates a monolayer of uniformly sized and shaped nanoparticles when immobilized on the silicon surface. X-ray diffraction shows that the biotemplated nanoparticles have the L₁₀ CoPt crystal structure, and magnetic measurements reveal stable, multiparticle zones of interaction, similar to those seen in perpendicular recording media. This is the first time that the L₁₀ phase of CoPt has been formed without high temperature/vacuum treatment (e.g., annealing or sputtering) and offers a significant advancement toward developing environmentally friendly, biotemplated materials for use in data storage.

1. Introduction

Historically, the density of data that can be stored on a disk drive has increased in a similar manner to Moore’s law.¹ This rapid growth rate has been achieved by developing new materials and systems that are able to store increasingly higher densities of data. Hard disks consist of layers of nanostructured magnetic materials that are able to reliably store bits of information.² High quality and uniformity are essential to ensure that the magnetic nanoparticles (MNPs) used to create recording surfaces can store data with high fidelity (i.e., low error rates). This is because MNPs with a uniform size, shape, and crystal structure have a uniform magnetic response.² High coercivity is also essential to ensure that the recorded bits are not easily demagnetized, providing stability and integrity in the recorded data.² Platinum alloys of cobalt and iron with the L₁₀ texture are excellent candidates for this purpose. This is because crystallographically aligned thin films of these particles have an extremely high out-of-plane magnetic anisotropy, which is ideal for use in high density perpendicular magnetic recording.⁴ Fabrication of such films usually requires high temperatures (≈ 500 °C) and bespoke, high vacuum sputtering equipment to achieve the L₁₀ crystal structure. These requirements mean that all of the other materials used in the construction of hard disks are also able to withstand such treatment, and is both economically and ecologically expensive.⁴,⁵ As such, we have turned to biomineralization to address some of these financial and environmental drawbacks. In biomineralization, proteins template the formation of a range of complex, hierarchically ordered materials under mild, aqueous conditions to form inorganic–organic composite tissues.⁶ Naturally occurring biominerals include calcite in shells,⁷ silica in sponges,⁸ and diatoms,⁹ hydroxyapatite in teeth and bones,¹⁰ and magnetic particles in magnetotactic bacteria.¹⁶,¹¹ Biomimics often have significantly enhanced properties when compared to their nonbiotemplated counterparts,¹² including: increased toughness (calcite shells),¹³ light guiding properties (silica sponge spicules),¹⁴ or maximized magnetic moment (magnetite chains in bacteria).¹⁵ It was previously shown that Mms6, a biomineralization protein from a magnetotactic bacterium, could be used to form a layer of biotemplated magnetite MNPs on a patterned...
surface. More recently, increased coercivity of patterned, biotemplated magnetite was achieved by doping with cobalt. Unfortunately, the magnetic hardness of magnetite (and cobalt-doped magnetite) is not high enough for use as the recording layer in current data storage applications. The high coercivity materials that are used in magnetic data storage are not known to be biomimimized by any organisms in nature. However, peptide sequences that are able to bind and template the formation of non-naturally occurring materials under mild reaction conditions have been developed. Synthetic biology techniques, such as rational design, computational modeling, and biopanning, have been used to find and optimize sequences that are able to bind to and biotemplate the formation of materials such as gold, silver, platinum, platinum alloys, palladium, titania and semiconductor nanomaterials.

Biopanning allows researchers to explore a vast parameter space of peptide binding motifs during the directed evolution of a library of up to $10^{15}$ different peptide sequences. Randomly generated peptide sequences are displayed on viral or bacterial hosts, which are incubated with the target material. After stringent washing, the remaining bound peptides are collected, amplified, and re-exposed to the target 3–5 times. This allows the researcher to direct the evolution of the library to identify peptide sequences that bind strongly to the target.

Previously, a gold and silica dual affinity peptide (DAP) was used to pattern nanoparticles and to form thin films of electrically conductive gold. In this work, our DAP sequence consists of a motif that strongly binds to silica (HPPMNASHFPHMI, biopanned by Eteshola et al.) and another that biotemplates CoPt (KTHEIHPHLH, biopanned by Klem et al.) connected via a flexible linker (GSG), the peptide design is summarized in Figure S1 (Supporting Information). Originally, the L1$_0$ CoPt phase was not biotemplated by the CoPt peptide sequence, but achieved by post-biominalization annealing at 650°C, and was not templated as a monolayer on a surface. The biotemplating system presented here has been optimized to form a closely packed, uniform, magnetically interacting monolayer of biotemplated L1$_0$ CoPt MNPs onto silicon surfaces. This is the first time that L1$_0$ CoPt (a material that could be used in high density perpendicular recording) has been formed at room temperature and without using any high temperature processing. As the L1$_0$ CoPt MNPs are templated as a monolayer onto a surface, this is far more amenable for use in recording when compared to MNPs biotemplated from a bulk solution. As such, this work offers a significant step toward the development of environmentally friendly, biotemplated magnetic materials for use in data storage.

### 2. Results

#### 2.1. Surface Biominalization

First, the biotemplating system was optimized to maximize the packing density of MNPs biotemplated onto the silicon surface. The density of particles templated onto the surfaces was quite low when the silicon substrate was incubated for 1 h in a buffered solution of DAP prior to metallization (Figure S2, Supporting Information, Table 1, average of 85 ± 10 particles µm$^{-2}$). These particles are not packed together closely enough to magnetically interact with each other, so their packing is insufficient to allow for the recording of data. In an effort to increase the packing density of MNPs further, silicon was microcontact printed with a poly dimethyl siloxane (PDMS) stamp that had increasing levels of peptide loading (Figure 1).

When the stamp is inked and dried once, the distribution of particles biotemplated by the DAP onto the silicon surface is inhomogeneous, and there are even fewer particles than seen for the surface functionalized with peptide from solution (just 13 ± 4 particles µm$^{-2}$). It was not possible to quantify the coverage of DAP on the surfaces investigated prior to metallization (e.g., using ellipsometry) as the peptide layer does not form a single layer with a consistent fixed thickness, but instead is unevenly distributed on the surface. This patchy, low coverage is most likely to be due to sparse and inconsistent transfer of the peptide from the stamp to the surface prior to mineralization. Therefore, the consistency and amount of peptide transferred to the surface was improved by increasing the loading of peptide onto the stamp. Figure 2 shows surfaces contacted with stamps that were inked with peptide two, eight, and ten times. In all cases, the stamps were contacted with the surface for 1 min prior to metallization (for detailed methods, see the Supporting Information). When the stamp was inked two times, there was patchy and sparse mineralization (349 ± 319 particles µm$^{-2}$). As the number of inking rounds increases, so does the packing density of the biotemplated particles. At 8 inks, there is still variability in the density of biomimialized particles on the silicon surface (365 ± 226 particles µm$^{-2}$). When inked with peptide ten times, a uniform, densely packed monolayer of particles is biotemplated onto the surface (707 ± 174 particles µm$^{-2}$). These data demonstrate that physical, controlled contact with a stamp bearing a high peptide loading (10 inks) onto the surface is essential to ensuring a uniform densely packed layer of biotemplated nanoparticles is formed. Therefore, samples for further characterization were all inked 10 times prior to mineralization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle density [particles µm$^{-2}$]</th>
<th>Standard deviation [particles µm$^{-2}$]</th>
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<tr>
<td>10 inks</td>
<td>707</td>
<td>174</td>
</tr>
<tr>
<td>8 inks</td>
<td>365</td>
<td>226</td>
</tr>
<tr>
<td>2 inks</td>
<td>319</td>
<td>319</td>
</tr>
<tr>
<td>1 ink</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>From solution</td>
<td>85</td>
<td>10</td>
</tr>
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#### 2.2. Imaging and Elemental Analysis of Biotemplated Surfaces

Uniformly sized single domain MNPs are desirable for use in data storage applications, as they exhibit a consistent magnetic behavior. L1$_0$ CoPt MNPs are thermally stable above a diameter of about 5 nm, and are able to maintain a single magnetic domain up to ~100 nm diameter. The 10 inks surface biotemplated particles have a narrow size distribution at the lower
end of this single domain size limit (17 ± 9 nm, Figure 3 and Table 2). This means that these surface biotemplated nanoparticles are ideally positioned within the lower end of this single domain zone. When the stamp was inked once with the DAP, slightly larger particles with a narrow size distribution were templated (22 ± 8 nm), again within this single domain size zone. Both of the surface biotemplated examples have far more equidimensional particles (i.e., with an aspect ratio close to 1) than either of the control samples (1 ink = 0.87 ± 0.09 and 10 inks = 0.88 ± 0.08) indicating that the surface immobilized CoPt–DAP is able to exert control over both the size and shape of the particles it templates at room temperature.

As controls, particles biotemplated from a bulk solution, both in the presence of 10 µg mL⁻¹ peptide (bulk DAP) and with no peptide (bulk), have also been analyzed. As expected, non-biotemplated bulk particles have the broadest size (5 ± 5 nm) and shape (aspect ratio 0.84 ± 0.11) distributions. They also form supra-particle clumps, most likely due to their broad grain size distribution,[32] which may be hollow spheres.[33] When the DAP is present in the bulk solution, there is a shift to a smaller grain size with a narrower distribution (4 ± 2 nm), and the particles are of a more elongated shape (aspect ratio 0.82 ± 0.11). There is also a clear lack of self-assembly into multiparticle structures, which may be due to the narrower size distribution and the coating of peptide which is likely to cap the bulk biotemplated particles.

Energy dispersive X-ray (EDX) spectra and maps were recorded for the 10 ink sample (Figure 4). The maps show that the cobalt and platinum are colocalized in the biotemplated particles. San et al. found that a 1:1 ratio of Co:Pt in the mineralization solution led to a ≈36:64 ratio in the biotemplated particles.
CoPt MNPs in protein cage biotemplated CoPt.[21b] The ratios of the reactants (cobalt:platinum:borohydride) were optimized to achieve the 1:1 ratio of L1₀-structured CoPt in the surface biotemplated MNPs. An excess of cobalt to platinum ions (3:1) in the mineralization solution allowed the surface immobilized peptide to template CoPt in a 55:45 ratio (Table 2), which is very close to the desired 50:50 ratio of L1₀ CoPt. EDX spectra were also recorded in the transmission electron microscope (TEM) to characterize the elemental composition of the control particles. Quantification of the cobalt and platinum ratio in bulk templated particles showed that, in the absence of peptide, the stoichiometry of the particles reflects that of the mineralization solution (Co:Pt, 76:24), Figure S3 (Supporting Information) and Table 2. The peptide templated particles from the bulk solution show a lower proportion of cobalt (Co:Pt, 46:54), which is close to the 50:50 ratio of L1₀ CoPt. Therefore, whether attached to the surface, or dissolved in the bulk solution, the DAP is able to control the stoichiometry of the biotemplated nanoparticles to form a desired ≈1:1 ratio of metallic Co to Pt from this aqueous metallization system at room temperature.

2.3. Crystallinity of Biotemplated CoPt

The X-ray diffraction (XRD) spectrum of a clean silicon wafer (Figure 5, and Figure S4 and Table S1, Supporting Information) shows peaks for silicon and the native oxide layer on the silicon. The 10 inks sample spectrum shows reflections that are due to the substrate (silicon and silicon oxide). In addition, there are peaks from the biotemplated nanoparticles, which can be clearly distinguished, and therefore their crystallographic origin can be assigned (Figure 5 and Table S1, Supporting Information). In L1₀ CoPt, segregation of Co and Pt stacked along the (001) direction creates a tetragonal distortion, which corresponds to the easy axis of magnetization for this material.[5c] Excitingly, for the 10 inks biotemplated sample, there are peaks at $2\theta = 25.80^\circ$ and $33.13^\circ$ that correspond to L1₀ CoPt (001) and (100) planes, respectively. Their crystallographic origin can be assigned (Figure 5 and Table S1, Supporting Information). In L1₀ CoPt, segregation of Co and Pt stacked along the (001) direction creates a tetragonal distortion, which corresponds to the easy axis of magnetization for this material.[5c] Excitingly, for the 10 inks biotemplated sample, there are peaks at $2\theta = 25.80^\circ$ and $33.13^\circ$ that correspond to L1₀ CoPt (001) and (100) planes, respectively. There is also an indication of a broad peak $2\theta = 40.52^\circ$ (triangle, Figure 5) that best fits the CoPt (111) peak. The low coercivity A1 phase of CoPt shows (111), (200), and (220) peaks.[5a] The study of Yu et al.[5a] demonstrates that annealing at 650 °C is required to achieve (001) and (110) L1₀ peaks in their system, and splitting of the (200) and (220) peaks is used to confirm L1₀ phase formation. It is likely that, if the CoPt (200) peak at $2\theta = 70.12^\circ$ is present in the 10 inks biotemplated sample, it is obscured by the large Si (400) peak at $2\theta = 69.03^\circ$ from the silicon substrate. Unfortunately, due to the small peak size from the biotemplated CoPt particles, and position of the Si (400) peak, it was not possible to

Table 2. Summary of grain size, grain shape, and elemental analysis from EDX measurements for surface biotemplated CoPt nanoparticles (10 inks and 1 ink) and appropriate controls (peptide in bulk and bulk particles). Details of the measurements and the calculation of associated errors are in the Supporting Information. The ratio of Co:Pt is calculated from the EDX spectrum using the EDX analysis software on the respective TEM or SEM.

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<tbody>
<tr>
<td>10 inks</td>
<td>17</td>
<td>9</td>
<td>0.88</td>
<td>0.08</td>
<td>55:45</td>
</tr>
<tr>
<td>1 ink</td>
<td>22</td>
<td>8</td>
<td>0.87</td>
<td>0.09</td>
<td>n/a</td>
</tr>
<tr>
<td>Peptide in bulk</td>
<td>4</td>
<td>2</td>
<td>0.82</td>
<td>0.11</td>
<td>46:54</td>
</tr>
<tr>
<td>Bulk</td>
<td>5</td>
<td>5</td>
<td>0.84</td>
<td>0.11</td>
<td>76:24</td>
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Figure 3. Representative electron microscopy images of the nanoparticles formed in this study. a) TEM images of bulk precipitated particles which have agglomerated into supraparticle clusters, and b) particles templated by the peptide in the bulk solution which are far more dispersed. c) Representative SEM images of surface contacted with a stamp that was inked with peptide once (1 ink) and d) ten times (10 inks), after mineralization with CoPt. There is a far lower density of particles biotemplated onto the surface contacted with the stamp inked once when compared to the surface contacted with a stamp inked 10 times. e) Grain size distributions and f) aspect ratios of: bulk (blue no fill), peptide in bulk (green solid fill), 1 ink (gray rising diagonal fill), and 10 inks (black descending diagonal fill).
determine if there is a splitting of the (200) and (220) peaks. In heat-treated CoPt films, high intensities of the (001) and (110) peaks when compared to the reflections due to A1 ordering (e.g., the (111) peak), indicate a high degree of L10 ordering.\(^5\) In L10 FePt, the absence of the (111) reflection is used to show that these films are very strongly L10 ordered.\(^4\) Therefore, the higher intensity of the (001) and (100) peaks in the surface biotemplated samples, when compared to the putative (111) CoPt peak, strongly supports the presence of the L10 rather than the A1 phase in the surface biotemplated CoPt. This is the first time that this L10 phase has been formed at room temperature without the need for any subsequent annealing, which is promising for its use in developing biotemplated MNPs.

Bulk precipitated controls both show strong peaks for CoPt\(_3\), which is not the desired L10 CoPt phase. This was unexpected, based on the evidence from the EDX spectra discussed above. It may be that, despite the excess of Co\(^{2+}\) in the mineralization solution, CoPt\(_3\) is more likely to form a crystalline phase under the reaction conditions optimized for surface biominalization of CoPt. Other cobalt rich phases may form amorphous or poorly crystalline coatings on the CoPt\(_3\). This would allow high levels of cobalt to show up in elemental EDX analysis, but more platinum rich species to be indicated by the crystallographic XRD data. Interestingly, there is an indication of a Co\(_2\)O\(_4\) phase in the bulk precipitated particles, which is absent in the peptide bulk tempered control. This is most likely to be due to surface oxidation of the non-biotemplated particles. This indicates that the CoPt–DAP remains bound to the particle surface when used in the bulk mineralization solution, offering protection against aerial oxidation. As there are no peaks for CoPt\(_3\), or oxidized Co\(_2\)O\(_4\) phases from the surface biotemplated CoPt nanoparticles, these data support the stability of the L10 CoPt surface biotemplated MNPs against transformation to CoPt\(_3\), or undesired oxidation by exposure to air respectively.

2.4. Magnetic Properties of Biotemplated L10 CoPt

Vibrating sample magnetometry (VSM) shows that the surface biotemplated particles have a ferromagnetic hysteresis at room temperature (Figure S5, Supporting Information). However, the saturation magnetization \(M_s\) of the sample, despite being very low \(\approx 3 \times 10^{-4}\) emu, is slightly higher than that estimated based on the volume of
To conclusively demonstrate that the magnetic interactions are solely due to the magnetic interaction of the particles with the tip, the direction of magnetization of the tip should be reversed and the same area scanned. If this were possible, the sign of the phase shifts should be reversed when the tip magnetization is reversed. Unfortunately, it was not possible to scan an area, reverse the magnetization of the tip, and then rescan the same area. This is because reversing the magnetization of the tip required removing the tip from the piezo head on the microscope. When the tip was re-mounted, it was not possible to reliably locate the same area to scan again. Figure S6 (Supporting Information) shows sequential MFM scans of the same area, with 90° rotation between them. These plots demonstrate that the areas of magnetic attraction and repulsion have the same shapes, sizes, and magnitudes of interaction in successive scans in different scan directions, making them unlikely to be due to artefacts.

3. Discussion

3.1. Size and Shape Control of Surface Immobilized CoPt–DAP

This work reports the formation of biotemplated L1₀ CoPt on a surface at room temperature for the first time. This material has the potential to be used in high density data storage, and the L1₀ phase has not been formed without the need for post-biotemplating high temperature processing before. These data demonstrate that, when there is a high loading of the CoPt–DAP on the stamp, the peptide is able to biotemplate a consistent layer of densely packed particles onto the stamped silicon surface. It is likely that more peptide is functionalized onto the surface by microcontact printing for the 10 ink samples than for the 1 ink sample. This would lead to more particle nucleation sites being more closely packed together on the substrates with higher peptide loadings. This close packing would also provide less room for maturation, creating smaller, more closely packed biotemplated particles on the 10 inks surface. This would explain the higher density of smaller particles that are observed on the 10 inks surface when compared to the samples that had less inking. These grain size data also show that, when densely packed on the surface, the peptide is able to exert significant control over the size and shape distribution of the nanoparticles biotemplated on the surface, when compared to the particles templated in the bulk solution. Close packing of the peptide on the solid surface may stabilize the biotemplating action of the DAP, allowing it to biotemplate uniform, equidimensional particles (Figure 3c,d). The particle size and distribution of the surface biotemplated nanoparticles (17 ± 9 nm) is above the superparamagnetic (SP) size limit for L1₀ CoPt (~5 nm), which is promising for use in data storage applications.

When the peptide was used in the bulk mineralization solution as a control, the elongation of the particles that are observed may be due to the lack of a surface to stabilize the biotemplating peptide during metallization, as well as the presence of the SiO₂ binding portion of the DAP. Display of repeats of biotemplating peptides on viral coats causes close packing of the peptides, and is thought to stabilize and enhance the biomineralization action and crystallographic alignment capabilities of semiconductor biotemplating peptides. It is likely that surface immobilization of the DAP creates a similar close packing of the CoPt biotemplating peptide on the surface, which may have similar stabilization effects on the
biotemplating ability of the peptide. The majority of the SiO₂ binding portion of the DAP is probably not interacting with the mineralization solution when it is immobilized onto a surface, as it is this section that should be in contact with the substrate rather than the metallization solution. However, the whole DAP sequence should be able to interact with the mineralization solution in the formation of the bulk peptide control. Also, the biotemplating peptide is only able to interact with the underside of the growing MNPs when immobilized onto the surface. In a bulk solution, the biotemplating peptide is able to surround all sides of a growing particle, and cap growth in all directions. On a surface, the potential to limit growth is diminished, as the peptide can only bind to facets on the bottom of the growing particle. Therefore, the peptide is probably only able to control the initial nucleation and growth of the MNPs on the surface by binding to the underside of the nucleating MNPs. Any subsequent growth of the MNPs on the surface is likely to be crystallographically aligned with the nucleated and growing MNP, but this growth cannot be capped by the peptide binding to the sides or top of the growing MNP. Similar enhancement of particle size can be seen in a completely different mineralization system: magnetite and cobalt doped magnetite MNP growth on surfaces biotemplated by the biominer-alization protein Mms6.⁶¹,¹⁷ This difference in which parts of the sequence are able to interact with the metallizing solution during nanoparticle formation could lead to the observed differences in particle morphology and size between the surface immobilized and bulk solution peptide templated MNPs.

3.2. Crystallographic Evidence for L₁₀ CoPt Formed at Room Temperature

The crystallinity data shows that the DAP is able to biotemplate the L₁₀ phase, rather than the lower energy A₁ phase, or CoPt₃, which forms from the bulk solution at room temperature. The surface immobilized biotemplating peptide is probably able to lower the activation energy of the formation of the L₁₀ CoPt phase from aqueous solution, thus favoring the formation of the higher energy L₁₀ phase. Mao et al.¹⁰ propose that close packing of biotemplating peptides (in their case on a viral coat protein) enhances the biotemplating function of their mineralization peptides and allows for crystallographic alignment of the biotemplated nanoparticles. The close packing of the DAP on the silicon surface may enhance the crystallographic alignment and templating capabilities of our biotemplating peptide. As discussed above (Section 3.1), the peptide is likely to only be able to bind to the underside of the MNPs. This means that capping of the peptide cannot be responsible for preventing oxidation of the surface biotemplated MNPs. A similar resistance to oxidation has been observed in magnetite biotemplated on surfaces by the Mms6 protein in previous work.¹⁶,¹⁷ It is possible that the high quality of the biotemplated L₁₀ CoPt MNPs is able to form outer facets that are able to resist oxidative attack, and thus be stable against alteration by air.

Recent work has shown that the binding of biotemplating peptides to specific facets of platinum is crucial for these peptides to control the shape of the Pt nanoparticles that are formed.²⁰a,²⁰b,²⁰d It is reasonable to assume that similar specific binding of the biopanned CoPt sequence [KTHEIHSPLLHK]²¹a to a distinct L₁₀ CoPt facet is able to direct the growth of this highly ordered phase. The CoPt biotemplating peptide may also be able to bind ions and/or prenucleation clusters of cobalt and platinum, organize them into the tetragonal L₁₀ structure and facilitate their reduction to metallic CoPt when bound to the surface. The peptide may also be able to do this in the bulk solution, but a larger excess of cobalt, or other alterations to the reaction conditions (which are optimized for surface mineralization), may be necessary for this to occur. It should be possible to probe the interactions of biomolecules, such as the DAP, with specific L₁₀ CoPt surfaces (e.g., (100), (110) or (220)), and to compare this to binding to A₁ CoPt surfaces. Computational modelling of the peptides interacting with the bimetallic L₁₀ CoPt surfaces could be employed to elucidate which peptides in the sequence are important for binding to specific facets, in a similar manner to computational studies that have explored biotemplating peptide binding to specific monometallic gold²⁷ and platinum²⁰d surfaces. These studies have been used to gain great insight into the mechanisms and specificity of materials binding by these gold and platinum biotemplating peptides, and similar techniques could be used to study how and where biotemplating peptides bind to L₁₀ CoPt to template its growth.

3.3. Magnetic Properties of Surface Biotemplated L₁₀ CoPt

The nanoscale magnetic behavior of the surface biotemplated MNPs is complex, with different sizes and shapes of zones of repulsion and attraction that extend over multiple particles. Interestingly, the shape, size, and position of the multiparticle magnetic zones appear to be stable at room temperature. Such patterns arise naturally from the demagnetization of magnetic thin films. The size and shape of clusters that have similar magnetization depend upon the magnetostatic and exchange interactions between particles.¹³ The size and shape of clusters have similar magnetization depend upon the magnetostatic and exchange interactions between particles.¹³ In 2D assemblies, these interactions, and the resulting cluster size, are very strongly determined by the particle size and spacing.³⁸ This observation of nanoscale regions with stable perpendicular magnetization is promising for the use of biotemplated CoPt in magnetic data storage, as a bit of information is usually recorded across a number of particles.²⁵ Thus, this ability of these surface biotemplated L₁₀ CoPt MNPs to stably maintain their magnetic orientation at room temperature indicates that they could be developed for use in magnetic data storage applications.

Electron holography and Fresnel–Lorentz microscopy has been used to image multiparticle magnetic domains in closely packed layers of magnetite nanoparticles.³⁹ They found that the shape of the multiparticle domains that formed in the magnetcite MNP assemblies is strongly dependent on the macroscopic shape of that assembly.³⁹ In previous work with ferromagnetic magnetite and cobalt-doped magnetite biotemplated onto surfaces, alignment and elongation of multiparticle zones of magnetic attraction and repulsion parallel to the long axis of the assembly can be observed using MFM.¹⁶,¹⁷ For the surface templated L₁₀ CoPt MNPs presented in this work, the multiparticle zones do not appear to align significantly with the edges of the scored areas (Figure 6b and Figure S6, Supporting
Information). This could be due to the lack of c-axis alignment that is inferred from the XRD and VSM measurements. It may also be that nanoscale interactions between neighbors of particles with random crystallographic orientation are dominating over any shape anisotropy exerted by the microscale scored boundaries. This would lead to the shape and size of the multiparticle zone system being dependent on slight variations in film heterogeneity (e.g., particle packing and spacing) rather than on any microscale shape features.

In sputtered or annealed films, out-of-plane c-axis alignment ensures high perpendicular magnetic anisotropy, making these layers suitable for recording. In films with out-of-plane c-axis alignment, the (001), (110), (200), and (220) peaks are observed in XRD. Our biotemplated film shows L1₀ CoPt (001), (100), (101), and (002) reflections (the (200) and (220) peaks may be obscured, see Section 2.3 above). This indicates that our biotemplated L₁₀ CoPt MNPs are not aligned in the same orientation as the sputtered films (e.g., there is no (110) reflection). This different alignment may explain why there is not a measureable coercivity for the surface biotemplated MNPs when measured in VSM. Hysteresis loops of sputtered CoPt with misaligned grains can show loops with reduced coercivity depending on the direction in which the external field is applied. As it was only possible to measure the magnetization of the samples in the out-of-plane direction, it may be that the c-axis of the film is aligned in plane, or in some other orientation.

Greater understanding of the facet specificity of a range of biotemplating peptides for L₁₀ CoPt (discussed above), could allow the development of peptides that are able to perpendicularly align the c-axis, e.g., by binding to the (110) plane, and create high coercivity biotemplated L₁₀ CoPt. Klem et al. found the CoPt templating section of the DAP by biopanning, but were unable to fully achieve the L₁₀ CoPt phase without annealing the biotemplated particles. They displayed the peptide sequence within a heat-shock protein cage, which could act as a barrier to diffusion of the reactants to the biotemplating sequence on the interior. They also performed their mineralization at room temperature using a peptide biotemplate for the first time. The biotemplating peptide affords excellent control over the size and shape of the MNPs formed when immobilized onto a surface, and our surface biotemplated L₁₀ CoPt are above the SP size limit for L₁₀ CoPt. The MFM data clearly shows that the surface biotemplated MNPs form multiparticle zones of magnetic interactions which are stable at room temperature. This stability is promising for the use of these biotemplated surfaces to develop biotemplated magnetic data storage. We believe that, in tuning the particle packing density by a controlled increase in the peptide loading to the surface, it should be possible to tailor the size of the surface biotemplated particles. Although the sputtered L₁₀ platinum alloy films do show extremely high coercivity, a number of the sputtered particles are below the SP size limit. These smaller particles are not able to maintain their magnetic orientation at room temperature in the absence of an applied field, so it is very easy to switch their direction of magnetization. These heterogeneities can act as nucleation points for demagnetization in recording layers, leading to loss of data (i.e., poor integrity), especially in the smaller bit sizes required in high density data storage. Therefore, biotemplated systems such as that presented here may offer not only a more environmentally friendly and cheaper alternative to conventional hard-disk data storage, but also one that is able to overcome this size control limitation seen in sputtered thin films of L₁₀ CoPt.

Unfortunately, the L₁₀ CoPt MNPs biotemplated onto our surfaces did not have a high out-of-plane coercivity, which probably due to a lack of alignment of the c-axis of the biotemplated MNPs based on our crystallographic data. Computational modelling of peptide interactions with surfaces could significantly increase our understanding of how and where specific peptides bind to different L₁₀ CoPt facets. This may even be able to identify peptides that are able to bind to key facets, as has been done for platinum and gold. Thus may be able to perpendicularly align the c-axis of L₁₀ CoPt for high density recording. Soft magnetic underlayers (e.g., ruthenium) are used to enhance the out-of-plane anisotropy of platinum alloy films. A biotemplating DAP could be designed to biotemplate this layer too. In sequence, these DAPs could be used to build a biotemplated magnetic thin film stack that incorporates such underlayers, all from aqueous solutions at

It may be possible to anneal our biotemplated films, as was done to achieve the L₁₀ phase in previous work, which may align the c-axis of the biotemplated MNPs out-of-plane. However, annealing often leads to agglomeration of adjacent particles, which can significantly increase particle sizes and size distributions, and thus introduce undesirable heterogeneity. Also, annealing a biotemplated film removes many of the advantages of the biotemplating process (e.g., low temperature, low energy, and low cost). Therefore, we propose a number of heat-free ways that these L₁₀ CoPt films could be improved for use in magnetic data storage, which are explored in the Conclusions section below.

4. Conclusions

This work demonstrates that L₁₀ CoPt can be formed on a surface at room temperature using a peptide biotemplate for the first time. The biotemplating peptide affords excellent control over the size and shape of the MNPs formed when immobilized onto a surface, and our surface biotemplated L₁₀ CoPt are above the SP size limit for L₁₀ CoPt. The MFM data clearly shows that the surface biotemplated MNPs form multiparticle zones of magnetic interactions which are stable at room temperature. This stability is promising for the use of these biotemplated surfaces to develop biotemplated magnetic data storage. We believe that, in tuning the particle packing density by a controlled increase in the peptide loading to the surface, it should be possible to tailor the size of the surface biotemplated particles. Although the sputtered L₁₀ platinum alloy films do show extremely high coercivity, a number of the sputtered particles are below the SP size limit. These smaller particles are not able to maintain their magnetic orientation at room temperature in the absence of an applied field, so it is very easy to switch their direction of magnetization. These heterogeneities can act as nucleation points for demagnetization in recording layers, leading to loss of data (i.e., poor integrity), especially in the smaller bit sizes required in high density data storage. Therefore, biotemplated systems such as that presented here may offer not only a more environmentally friendly and cheaper alternative to conventional hard-disk data storage, but also one that is able to overcome this size control limitation seen in sputtered thin films of L₁₀ CoPt.
room temperature. Such layering may significantly enhance the out-of-plane coercivity of the biotemplated magnetic thin film, which would allow it to be used for recording.

It is our goal to demonstrate that materials templating peptides have the ability to form the components necessary to build devices, such as hard disks, without the need for high cost, high temperature, and high energy processing. In developing peptide templated magnetic data storage, it may be necessary to combine a range of different biotemplated materials. There is a vast array of biosystems that can be adapted for use in industry, and in the development of future consumer products.[8] The ultimate step toward making biosynthesized devices a reality is to combine separate biotemplated components to build consumer devices. Researchers have begun to demonstrate that biotemplated and biosynthesized components; such as solar cells,[44] circuitry,[28] data storage (this work), fiber optics, andsumer devices. Researchers have begun to demonstrate that biotemplated and biosynthesized components; such as solar cells,[44] circuitry,[28] data storage (this work), fiber optics, andsumer devices. Researchers have begun to demonstrate that biotemplated and biosynthesized components; such as solar cells,[44] circuitry,[28] data storage (this work), fiber optics, andsumer devices. Researchers have begun to demonstrate that biotemplated and biosynthesized components; such as solar cells,[44] circuitry,[28] data storage (this work), fiber optics, andsumer devices.

X-Ray Diffraction (XRD): Spectra were recorded using a Brucker-AXS D8 series2 diffractometer, set to a Bragg Brentano Parafocussing Geometry. X-rays were generated at room temperature using a Cu Kα source at 40 kV. Monochromated X-rays pass through a 2 mm exit slit and an automatic divergence slit of 0.2°. Diffraction intensity was collected at 2θ between 10° and 80° on a Braun position sensitive detector (0.01° and 7.5 s step⁻¹). These data were processed using AXS Commander and EVA software.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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