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Magnetic Manipulation and Optical Imaging of an Active Plasmonic Single-Particle Fe—Au Nanorod

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Supporting Information

ABSTRACT: Superparamagnetic microbeads play an important role in a number of scientific and biotechnology applications including single-molecule force measurements, affinity separation, and in vivo and in vitro diagnostics. Magneto-optically active nanorods composed of single-crystalline Au and polycrystalline Fe segments were synthesized with diameters of 60 or 295 nm using templated electrodeposition. The Fe section was magnetically soft and had a saturation magnetization of approximately 200 emu/g, resulting in a 10-fold increase in magnetization relative to that iron oxide nanoparticles. The strong plasmonic response of the Au segment of the rod in both the longitudinal and transverse directions made it possible to detect the orientation of a single rod in a polarized light microscope with nanometer resolution. These nanorods provide significantly improved physical properties over iron oxide superparamagnetic beads, making it possible to simultaneously manipulate and monitor the orientation of biomolecules with well-defined forces at the nanometer scale.

INTRODUCTION

The application of magnetic forces to proteins, nucleic acids, and cells based on superparamagnetic materials has proven to be a powerful tool for working with biological systems. Superparamagnetic microbeads have been utilized for exceptionally high efficiency affinity separation,1–4 multidimensional single-molecule magnetic force measurements,5–8 and ultrasensitive in vitro and in vivo diagnostics.9–13 The micrometer size beads typically used in these applications are composed of iron oxide–polymer composites with a saturation magnetization between 2 and 18 emu/g, which allows pico-Newton forces to be easily applied to the beads using rare-earth permanent magnets. Each of these applications would benefit from the development of multifunctional particles that have improved magnetic and optical properties.14,15 Increasing the magnetization of the beads will allow higher magnetic forces to be generated for a given size particle, which is an important factor for large-scale affinity separation and higher force-temporal resolution magnetic tweezer measurements. Imparting improved optical activity to the particles will enable multiplexed sensing as well as higher spatial resolution single-molecule measurements.

Heterogeneous nanostructures have attracted significant interest due to their unique electronic, magnetic, optical, and catalytic properties.14,15 Several synthetic methods have been developed for creating cylindrical shaped nanoparticles, including vapor—liquid—solid growth,16 colloidal synthesis,17 and template-assisted deposition.18 Among these technologies, porous anodic alumina (PAA) membrane-based template synthesis has proven to be a powerful route for obtaining uniform segmented nanorods of defined shape and composition.19,20 Recently, trisegmented Au—Ni—Au nanorods have been synthesized and used for protein separation.21,22 The Au sections of these nanorods were optically active and promise to be highly useful for sensing and nanomanipulation.23–27 Unfortunately, the Ni segments of the nanorods retain some level of ferromagnetism that limits the utility of these materials for biotechnology applications. Fe nanoparticles have the potential to be magnetically soft and have a much higher saturation magnetization than Ni. It has proven to be difficult to produce stable Fe sections due to the relatively high reactivity of Fe compared with other metals such as Au, Pt, and Ni, although a group has recently described the synthesis of gold—iron oxide rod arrays.28 In this paper, we report the fabrication and characterization of Fe—Au nanorods formed through the electrodeposition of Fe and Au in PAA templates. The Fe and Au segments of lengths \( l_{Fe} \) and \( l_{Au} \) were synthesized by sequential electrodeposition of the metals in PAA membranes of defined diameter \( d \) by controlling the time of deposition of each section. Three classes of nanorod shapes (Scheme 1) are described in this paper:

(1) Wide rods with \( d = 295 \pm 25 \) nm, \( l_{Fe} = 915 \pm 44 \) nm, and \( l_{Au} = 1056 \pm 62 \) nm.

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Dispersed Fe (3 M, Aldrich) and fuming nitric acid (100%, Aldrich), respectively. and Fe required 0.003 and 0.009 C, respectively. The PAA membrane monitoring the charge during deposition, and 100 nm segments of Au and AgCl). The segmental length of each element was controlled by

The integration of magnetic and optical elements into a two-segmental nanorod combined shape anisotropy and multifunctionality into one entity. This specific set of nanorod dimensions was chosen to fix the Fe—Au segment length ratio to approximately 1:1 while changing the length to diameter ratio from approximately 3:1 to 2:1.

EXPERIMENTAL SECTION

Synthesis of PAA Templates. The PAA templates were synthesized by a three-step anodization method, modified from the method established by Masuda et al. A high-purity (99.999%) piece of aluminum (Aldrich) was electropolished in a mixture of 5 vol % sulfuric acid (98%, Aldrich), 95 vol % phosphoric acid (85%, Aldrich), and 20 g/L chromium oxide (Aldrich) at 20 V and 85 °C for 2 min. This polished piece of aluminum was anodized in 0.42 M oxalic acid (Aldrich) at 40 V and 0 °C for 11 h. The alumina layer was removed from the sample using an aqueous mixture of chromium oxide, phosphoric acid, and water (45 g/L, 3.5 vol %, and 96.5 vol %, respectively) at room temperature for 5 h. A second 6 h anodization and 5 h stripping step was conducted under the same conditions as described above. A third 5 h anodization step produced highly ordered PAA template. The residue of the aluminum piece was removed by immersion in saturated mercury chloride aqueous solution for 4 h. The as-prepared PAA membrane was then immersed in 1 vol % phosphoric acid solution for pore widening for 10 min, resulting in a pore diameter of approximately 60 nm.

Synthesis of Fe—Au Two-Segmental Nanorods. The synthesis of segmented metal nanorods was based on the method developed by Martin and Moskovits. Briefly, a Au layer (ca. 200 nm) was sputtered on one side of the PAA template to serve as a working electrode in an electrochemical setup. An Ag/AgCl reference electrode and a Pt wire counter electrode were utilized to form a three-electrode configuration. The electrodeposition was controlled with a potentiostat/galanostat (2273, Princeton Applied Research). A Ag layer (ca. 2 μm) was first electrodeposited into the nanopores from a silver plating solution (around 28.7 g/L, Alfa Aesar) at a constant potential of —0.8 V (vs Ag/AgCl). The Au and Fe layers were deposited from a commercial electroplating solution (Orotemp 24 RTU, Technic Inc.) and a freshly made iron sulfate solution (FeSO₄·7H₂O, 120 g/L; boric acid, 45 g/L; ascorbic acid, 1 g/L, Aldrich), respectively, at —0.9 V (vs Ag/AgCl). The segmental length of each element was controlled by monitoring the charge during deposition, and 100 nm segments of Au and Fe required 0.003 and 0.009 C, respectively. The PAA membrane and Ag segment were removed with sodium hydroxide aqueous solution (3 M, Aldrich) and fuming nitric acid (100%, Aldrich), respectively. Dispersed Fe—Au nanorods were obtained after surface modification as follows: The nanorods were washed thoroughly with sodium hydroxide solution (0.01 M), deionized water, and ethanol (Aldrich). The particles were then functionalized with a poly(ethylene glycol) (PEG) monolayer by an overnight reaction of the rods with CH₃-PEG-SH solution (1 mg/mL, Rapp Polymer) in ethanol at 40 °C.

Electron Microscopy. The morphology and composition of the nanorods were evaluated by field emission scanning electron microscopy (FE-SEM; Hitachi S-4300) and energy-dispersive X-ray (EDX) spectroscopy. The structure of the individual segments of the nanorods was acquired by transmission electron microscopy (TEM; JEOL 2100), and the crystal structure was determined by selected area electron diffraction (SAED). The high-resolution TEM (HR-TEM) images were acquired by field emission TEM (FE-TEM; Titan 80-300, FEI). Figure S1 (Supporting Information) presents the top-view FE-SEM images of the as-prepared PAA templates before and after Au sputtering. Figure S2 (Supporting Information) presents the cross-sectional FE-SEM images of the as-deposited Fe—Au nanorods in PAA templates. Figure S3 (Supporting Information) presents the EDX elemental mapping in an aggregate. In Figure S4A (Supporting Information), the single-crystalline structure of the Au segment was elucidated in its SAED pattern with zone axis [111]. The typical diffraction rings in Fe SAED pattern revealed its polycrystalline structure. Figure S4B presents an HR-TEM image of the Fe—Au interface.

Magnetometry. The magnetic properties of the nanorods were analyzed by superconducting quantum interference device (SQUID) magnetometry (Quantum Design, MPMS XL 7T). Figure S6 (Supporting Information) presents how the magnetization of the Fe nanorod array was obtained. The ferromagnetic behavior of the Fe—Au—Ag—PAA—Si substrate and the diamagnetic behavior of the Au—Ag—PAA—Si substrate (as the background) are clearly shown in Figure S6A,B. After background subtraction, the magnetization of the Fe nanorod array (Figure S6C) was obtained, followed by a normalization process (Figure S6D). Figure S6D also presents criteria used to identify the effective anisotropy field (H_affective). Figure S6 presents how the demagnetizing factors for class I, II, and III nanorods were calculated. Demagnetizing factors are defined as N = (H_actual — H_applied)/M (here M refers to M (Oe) = 4πM (emu/cm³)). On the basis of this definition, the values of demagnetizing factors (N_l, longitudinal; N_r, transverse; ΔN, N_l — N_r), near saturation, were calculated.

Optical Microscopy. Polarization microscopy was carried out using a modified Nikon Eclipse 80i upright microscope equipped with a Nikon Digital Sight DS-Fi color charge-coupled device (CCD) camera, a 100 W Hg light source, and a 100× Nikon oil immersion lens with a numerical aperture (NA) of 1.49. Both the polarizer (p-preset) and analyzer (p-preset) had extinction ratios of 10000:1. Figure S8 (Supporting Information) presents a schematic setup of the transmission polarization microscope.

Acquisition of the images resulting in Figure 3B was carried out as follows. A small quantity of nanorods were dispersed in DFP mountant (VWR), and individual nanorods were located with the microscope operating in a nonpolarized mode, i.e., both polarization elements removed from the system. Images containing scattered light of altered polarization from the individual nanorods were acquired with the polarizing elements aligned 90° to each other, which eliminates almost all of the directly transmitted light. Both the polarizer and analyzer were rotated through a full 360° with images recorded at 10° increments. The images were acquired in a manual acquisition mode with identical camera settings (i.e., fixed exposure time, no gain, and no color filtering) to allow the images to be directly compared.

Analysis of the images to create Figure 3C was carried out as follows. A MatLab (Mathworks, Natan, MA) program was written to analyze the microscope images presented in Figure 3B. This program computed the effective intensity of the optical scattering from the nanorods. To achieve this, the program integrated the apparent intensity of the scattered light from a single nanorod and subtracted the background light level taken from an equivalently sized area adjacent to the nanorod. The process was repeated for all examined nanorod/polarization orientations for class I and II nanorods, resulting in the transfer intensity plot presented in Figure 3C.
RESULTS AND DISCUSSION

Figure 1A presents an E-SEM image of a cluster of class I nanorods that are naturally formed after removal of the template and the protective silver layer. The Fe and Au segments of the rods can be identified in this image by their apparent brightness, and it is clear that each segment is approximately 1000 nm in length and 295 nm in width. The inset graph in Figure 1A presents the EDX spectra collected on the aggregate of class I nanorods in which only Fe and Au elements can be identified. The EDX spectra confirmed that the rods were composed of equivalent quantities of Fe and Au and that the PAA template and Ag layer were completely removed from the rods. Figure 1B presents an SEM image and EDX spectrum of the class III nanorods, which appeared to be similar in shape and composition to the class I rods, but to have a much smaller length and diameter.

The crystal structure of each segment of the nanorods was determined with TEM and SAED. Figure 1C presents a TEM image of a representative class I nanorod in which the Au and Fe sections of the nanorod can be identified by their dark and light

Figure 1. Morphologies and crystal structures of the Fe–Au nanorods. (A, B) FE-SEM images of class I and III nanorods in which the dark Fe and light Au segments are clearly distinguishable. The inset graphs present the EDX spectra collected from these samples with corresponding atomic composition analysis. (C) TEM image of class I nanorods in which the light Fe and dark Au segments are clearly distinguishable. The inset SAED patterns of Fe and Au segments clearly identify the polycrystalline nature of Fe and single-crystalline state of the Au segments. (D) HR-TEM image of the Fe–Au interface of the class I nanorods.
The magnetic properties of the Fe–Au nanorods were characterized with a SQUID. Figure 2 presents the results of magnetization measurements performed on the nanorod arrays in the PAA membrane with the magnetic field oriented parallel and perpendicular to the longitudinal axis of the rods. These measurements reflect the properties of the Fe segment of the rods as the background magnetization of the Au–Ag–PAA membrane has been removed from the results presented in Figure 2. The hysteresis loops (Figure 2) indicated that all three nanorods were magnetically soft and had an easy axis that is oriented along their longitudinal direction. Table 1 summarizes the magnetic properties of the Fe nanorods and indicates that their saturation magnetization ($M_s$) was quite close to that of bulk Fe, which is 1750 emu/cm$^3$ or 220 emu/g.\textsuperscript{31}

An important feature of the magnetic properties of the Fe segment of the nanorods was that they were magnetically soft, which allowed the nanorods to be repeatedly used for magnetic separation without acquiring a residual magnetic moment. The hardness of the class I, II, and III nanorods was characterized by their squareness, i.e., the ratio between the remanent and saturation magnetization, $M_r/M_s$. The low levels of squarenesses of all the nanorods, i.e., $M_r/M_s < 0.1$, suggest that the Fe rods are composed of multidomain particles based on the criteria given by Dunlop.\textsuperscript{32} This behavior differs from that in previous studies of iron nanowires, which have focused on tuning the Fe grain structure to produce hard magnetic properties.\textsuperscript{33} The strong magnetic susceptibility, soft magnetic behavior, and relatively large size of the class I rods make them an ideal material for magnetic tweezers and diagnostic applications.

Although these nanorods possessed common levels of magnetic saturation and hardness, the anisotropic behavior of the longitudinal and transverse magnetization showed significant differences. The magnetization curves in Figure 2 illustrated that the class I nanorods were significantly less anisotropic than class II nanorods and that the class II nanorods had an anisotropy similar to that of the class III nanorods. Table 1 presents the anisotropy field factors for the nanorods, where $\Delta N$ is the demagnetization difference between the longitudinal and transverse directions of the nanorod. $H_{A,\text{shape}}$ is the shape anisotropy field, i.e., $H_{A,\text{shape}} = M_s \Delta N$, and $H_{A,e} = H_{A,\text{shape}}$ is the effective anisotropy measured directly from the hysteresis loops. The magnitude of $H_{A,\text{shape}}$ is sensitive to the aspect ratio and diameter of the rods, with a larger aspect ratio and smaller diameter leading to greater shape anisotropy, i.e., $H_{A,\text{shape}}(\text{class III}) > H_{A,\text{shape}}(\text{class I}) > H_{A,\text{shape}}(\text{class II})$. However, shape anisotropy does not fully account for the strong correlation between $H_{A,e}$ and diameter, i.e., $H_{A,e}(\text{class II}) > H_{A,e}(\text{class III}) > H_{A,e}(\text{class I})$. Magnetic anisotropy also results from the magnetocrystallinity, stress, and surface effect of the particles.

The Fe–Au nanorods were designed to be optically active, on the basis of the very strong plasmonic properties of gold nanowires,\textsuperscript{23,25} to allow not only their position but also their orientation to be determined. Figure 3A presents an image of well-dispersed, single class II Fe–Au nanorods that have been highlighted with white circles. The inset image shows a representative zoomed area of one of these nanorods. Despite the small dimension of class II nanorods, the gold and iron segments and their orientations can be identified through their optical signatures. The first image in Figure 3B presents an image of a much larger class I Fe–Au nanorod that was captured in bright-field polarization microscopy. This image confirmed that the sample is indeed a single isolated nanorod and also allowed for the clear identification of the substructure of the nanorod.

Systematic polarization microscopy was used to further characterize the optical properties of the gold segments of the.
Table 1. Magnetic Properties of the Fe Segment of the Class I, II, and III Nanorods

<table>
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<th>longitudinal</th>
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<td>$H_{\text{r}}^{11}$</td>
<td>$M_r$ (emu/cm$^3$)</td>
<td>$M_s$ (emu/cm$^3$)</td>
<td>$M_r/M_s$</td>
<td>$H_{\text{r}}^{11}$</td>
</tr>
<tr>
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<td>14.7 ± 0.7</td>
<td>1457 ± 73</td>
<td>0.01</td>
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<tr>
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<td>194</td>
<td>142 ± 7</td>
<td>1575 ± 79</td>
<td>0.09</td>
<td>150</td>
</tr>
<tr>
<td>III</td>
<td>226</td>
<td>107 ± 5</td>
<td>1654 ± 83</td>
<td>0.06</td>
<td>205</td>
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Figure 3. Optical characteristics of the Fe–Au nanorods acquired in transmission polarization microscopy. (A) Optical image of multiple, isolated class II Fe–Au nanorods (highlighted with white circles). The inset image presents a representative zoomed image of a single nanorod, in which the two segments can be identified despite the small dimensions of class II nanorods. (B) Transformation of the optical signatures of a single class I nanorod with illumination polarization. The top left image was captured in bright-field mode and allowed the Au and Fe segments to be clearly visualized with an intricate substructure. The next image presents a schematic of the nanorod defining the illumination polarization relative to the orientation of the nanorod. The subsequent images were taken in “dark-field” mode with the analyzer oriented orthogonal to the illumination polarization. (C) Polar plot illustrating the intensity of transferred scattered light through the system (radius axis) of class I (blue) and class II (red) nanorods as a function of the polarization angle ($\theta$). The longitudinal and transverse illumination polarizations have been defined with green axes.

The images in Figure 3B were acquired with linearly polarized transmitted light oriented at an angle $\theta$ to the longitudinal axis of the rod and the analyzer oriented 90° relative to the polarizer. This setup blocked the majority of the transmitted light that did not interact with the nanorod and therefore functioned similar to a dark-field microscope. The optical signature of the gold nanorod was characterized by the polarization-dependent change in the intensity of the two bright stripes, which is a result of optical effects associated with the cylindrical geometry of the rod, the plasmonic modes excited on the nanorod, the ultrahigh collection angle of the 1.49 NA objective lens, and the illumination geometry. The darker stripe along the middle of the rod’s longitudinal axis resulted from the shadow produced by the cylindrical rod when imaged in the transmission direction. In contrast, light coming from plasmonic modes, which have an altered polarization direction and are scattered diffusely from the edges of the rod, can be detected by the wide-angle collection of the objective lens and pass through the analyzer. It is exciting to note that the high numerical aperture and quality of the lens used in this study permitted us to image features of the plasmonic electromagnetic field distribution, i.e., plasmonic modes with details, which are otherwise typically only observable using near-field imaging techniques, e.g., three intensity maxima observable in the 90° orientation image in Figure 3B.

Figure 3C presents the intensity of the optical signature of the rods that was measured from the images in Figure 3B as a function of $\theta$. The minimum intensity was observed when the illumination polarization was oriented parallel to the longitudinal and transverse axes, i.e., $\theta$ of 0°, 90°, 180°, or 270°, and the maximum intensity was observed when the illumination polarization was oriented halfway between the longitudinal and transverse axes, i.e., $\theta$ of 45°, 135°, 225°, or 315°. The plasmonic contribution to this behavior can be understood by considering three exemplary orientations. First, when the polarization was aligned parallel to the longitudinal axis of the nanorod, i.e., $\theta$ of 0° or 180°, the longitudinal axis plasmon was excited at a maximum level. However, the scattering was polarized along the longitudinal axis and thus was almost completely rejected at the analyzer, resulting in the observed intensity minimum. Second, when the polarization was aligned perpendicular to the longitudinal axis of the nanorod, i.e., $\theta$ of 90° or 270°, the transverse axis plasmon was excited. Analogous to the previous case, upon scattering, this light had a polarization orientation aligned in the transverse direction that was rejected by the analyzer, resulting in the observed minimum. Third, consider now the case where the polarization was aligned halfway between the longitudinal and transverse orientations of the nanorod. In these cases, both longitudinal and transverse axis plasmonic modes were partially excited. However, as the resulting scattered light maintained the polarization defined by the plasmonic modes, the polarization lies at an angle of 45° or 135° to the polarizer and analyzer. When this light was analyzed, a relatively large portion of the light passed through the analyzer, maximizing the observed intensity. As presented in Figure 3C, the scattering behavior observed for both class I and class II nanorods followed the same trend. The relative intensity of light transferred through the polarization microscope provides a powerful technique that enables the orientation of subwavelength nanorods (class II or even smaller) to be defined in the far field without visualization of the Fe section of the rod (which is an alternative to the direct imaging of the class II nanorod orientation by the aid of the Fe section, as presented in Figure 3A).
The simultaneous magnetic manipulation and optical imaging of a single class I nanorod has been demonstrated in a detailed movie, available as part of the Supporting Information. It is clear that the plasmonic scattering behavior of the rod resulting from magnetic manipulation was consistent with the results acquired by variation of the angle of illumination polarization.

**CONCLUSIONS**

We have described the synthesis of Fe–Au nanorods that have high saturation magnetization, low remanence, uniform size, well-defined surface chemistry, and strong plasmonic activity. The simultaneous manipulation and imaging of a single nanorod has demonstrated the utility of these materials for magnetic tweezers measurements. A key result of this study is that the Fe nanorods have been synthesized with soft magnetic properties and a saturation magnetization that is an order of magnitude higher than that of iron oxide nanoparticles. These nanorods promise to significantly improve the performance of magnetic tweezers and high gradient magnetic separation. For example, the class I nanorods are capable of applying forces equivalent to those of 1 μm diameter iron oxide superparamagnetic beads, but their rotational and translational drag coefficients are between 1 and 4 orders of magnitude lower than those of the beads.34 The class II and III nanorods will produce significantly smaller forces than the class I rods but can be used to make even higher temporal resolution measurements. The second important result of this study is that the combined optical and asymmetric geometry of these nanorods made it possible to detect their position and orientation with exceptionally high resolution. The fact that the rods produced an optical signature that is proportional to their length and orientation makes it possible in principle to make measurements on single ligand—receptor pairs in three dimensions with nanometer resolution. Frequency-dependent scattering based on the geometry, size, and aspect ratio of the different nanorod classes has also been observed for gold nanorods.35,36 This suggests that it may be possible to tune the plasmonic response of specific nanorods for use in vitro and in vivo diagnostics if polarized illumination of a given frequency is employed. In this study, the nanorods were synthesized on a 0.1 cm2 PAA template, producing 10−100 μg of rods per run. Commercial production of 10 cm2 PAA membranes has been achieved; thus, we anticipate that the production of nanorods can be scaled to the milligram level by using 1−10 cm2 PAA templates and/or making multisegmented nanorods, i.e., (Ag−Au−Fe)n, n = 10−30.

**ASSOCIATED CONTENT**

 Supporting Information. Images and movies of the synthesis of PAA templates, synthesis and characterization of the Fe–Au nanorods, and demonstration of simultaneous magnetic manipulation and optical imaging of single nanorods. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**


