Supporting Information for

Self-Assembled Ferrimagnet-Polymer Composites for Magnetic Recording Media

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Experimental Section

Materials. Cobalt (II) acetylacetonate (97%), iron (III) acetylacetonate (99.99%), oleic acid (90%), oleylamine (90%), 1,2-hexadecanediol (90%), benzyl ether (99%), tetraethyl orthosilicate (99.99%), and ammonium hydroxide (30 wt%) were obtained from Sigma-Aldrich. Hexane, ethanol, and tetrahydrofuran were purchased from J. T. Baker. All the chemicals were used as received without any further purification. The PAA-b-PS diblock copolymers were synthesized according to the reported literature (Liu, G. et al *Chem. Mater*. **2005**, 17, 4985-4991).

Synthesis of Ferrimagnetic Oleic Acid Protected $CoFe_2O_4$ MNPs. 18 nm ferrimagnetic $CoFe_2O_4$ MNPs were prepared following a procedure reported by Sun et al.[11] Briefly, 2 mmol $Fe(acac)_3$, 1 mmol $Co(acac)_2$, 10 mmol 1, 2-hexadecaediol, 6 mmol oleic acid, 6 mmol oleylamine, and 20 mL of benzyl ether were mixed and mechanically stirred under a flow of N_2. The mixture was heated to 200°C for 2 h and then, under a blanket of N_2, heated to reflux (~ 300°C) for 1 h. The black colored mixture was cooled to room temperature by removing the heat sources. Under ambient conditions, 40 mL of ethanol was added to the mixture and a black material was precipitated and separated via centrifugation at 6000 rpm for 10 min. the black precipitate was dissolved in hexane with 0.1% oleic acid. The mixture was centrifuged at 6000 rpm for 10 min to remove any undispersed residue. The product was then precipitated with ethanol, centrifuged to remove the solvent, and dried in vacuum overnight. The average diameter of the $CoFe_2O_4$ MNPs is 6 nm with narrow size distribution. The as-synthesized 6 nm $CoFe_2O_4$ MNPs were further used as the seeds to grow larger particles. Typically, 2 mmol $Fe(acac)_3$, 1 mmol $Co(acac)_2$, 10 mmol 1, 2-hexadecaediol, 2 mmol oleic acid, 2 mmol oleylamine, and 20 mL of benzyl ether were mixed and mechanically stirred under a flow of N_2. 6 mL of the above synthesized 6 nm $CoFe_2O_4$ MNP hexane solution (15 mg/mL) was added. The mixture was first heated to 100°C for 30 min to remove hexane, and then increased to 200°C for 1 h. Under a blanket of N_2, the mixture was further heated to 300°C for 30 min. Following the same workup procedures, the monodispersed $CoFe_2O_4$ MNPs with a diameter of 15 nm were obtained. Finally, this seed mediated growth method

was repeated again to prepare 18 nm monodispersed $CoFe_2O_4$ FMNPs.

PAA-b-PS Surface Modification of Oleic Acid-coated 18 nm $CoFe_2O_4$ FMNPs. In a glass container under ambient conditions, 1mL of PAA_{33}-b-PS_{340} (MW: 37 K; PDI: 1.06) THF solution (10 mg/mL) was added to a dispersion of above synthesized 18 nm oleic acid-coated $CoFe_2O_4$ FMNPs (10 mg in 10 mL THF). The mixture was stirred magnetically for 18 h under room temperature. The PAA-b-PS modified particles were separated with a magnet and the solvent was decanted. The particles were washed three times with THF, ensuring removal of unbound polymers. The washed particles were dried in vacuum overnight for further characterization.

Preparation of Self Assembled and Magnetically Aligned $CoFe_2O_4$ FMNP Thin Films. The self assembled $CoFe_2O_4$ FMNP thin films were prepared by spin coating (speed: 3000 rpm/min) of polymer-modified $CoFe_2O_4$ FMNP toluene solution (2 mg/mL) on a one inch silicon wafer. The self assembled MNP thin films were subjected to alignment experiment with a magnetic field of 2800 Gauss.

Characterization Methods. FT-IR spectra of the $CoFe_2O_4$ FMNPs were recorded on a Thermo Nicolet NEXUS 670 FT-IR. Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min using a Perkin-Elmer TGS-2 instrument. Transmission electron microscopy (TEM) images were recorded on a Philips CM12 TEM (120 KV). A drop of $CoFe_2O_4$ FMNP solution was placed onto a carbon-coated copper grid and left to dry at room temperature. Scanning electron microscopy (SEM) images were recording on Hitachi S-4700 instrument. Magnetic measurements were carried out using an ADE Technologies DMS Model 10 VSM. PeakForce quantitative nanomechanical (QNM) analysis was conducted on Veeco instruments operating on a Dimension Icon scanning probe platform. The magnetic recording performance was conducted on a contact magnetic tester. The recording is performed with a hard-disk type head with separate write and read elements. The width of the write pole is 160nm and the width of the giant magneto-resistive (GMR) read element is 115nm. This head is scanned across the surface of the sample with a piezoelectric nanopositioning stage.

Essential magnetic recording characteristics are measured, such as the write voltage saturation and spatial frequency dependence of signal amplitude.

Figure S1. Hysteresis loops measured by VSM (298 K) of the 18 nm oleic acid-stabilized $CoFe_2O_4$ FMNPs

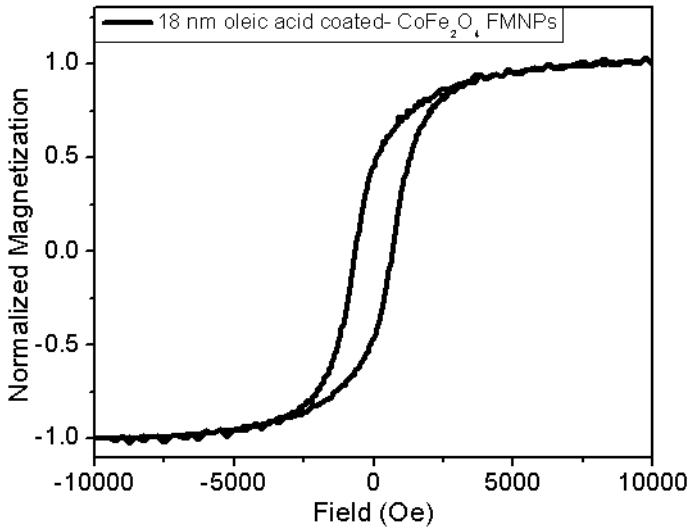

Figure S2. The picture shows the magnetic coupling interaction induced- nanoparticles aggregation; (a): fresh prepared 18 nm oleic acid coated- $CoFe_2O_4$ FMNPs hexane solution; (b): the nanoparticles solution after storing at ambient temperature for 7 days

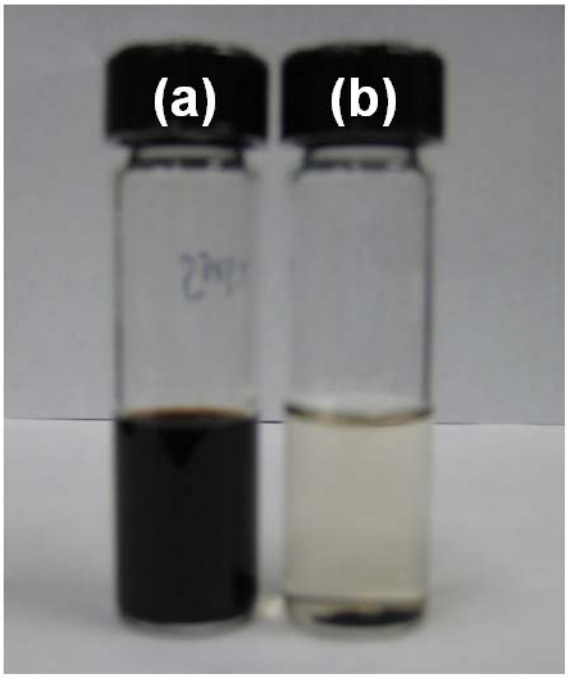

Figure S3. FT-IR spectra of 18 nm $CoFe_2O_4$ FMNPs before and after PAA_{33}-b-PS_{340} block copolymer modification

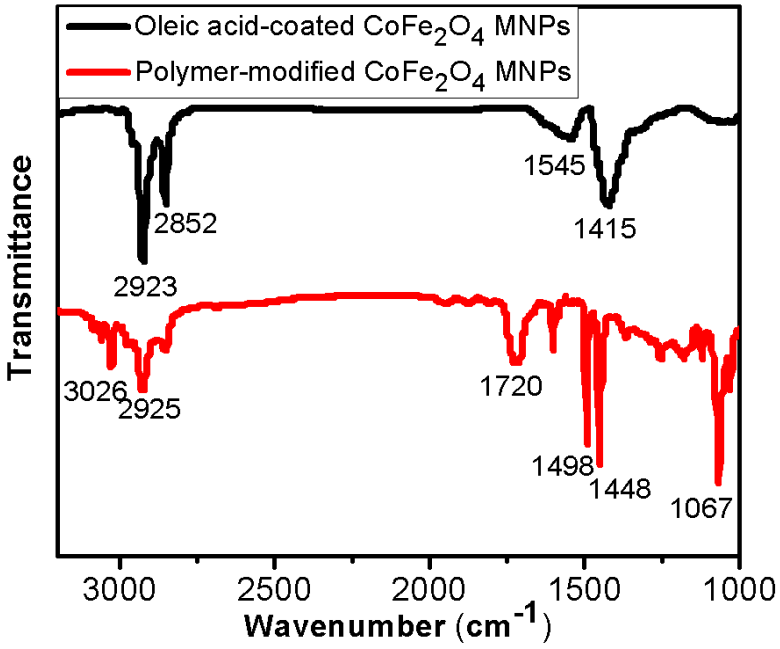

Figure S4. TGA analysis of 18 nm $CoFe_2O_4$ FMNPs before and after PAA_{33}-b-PS_{340} block copolymer modification

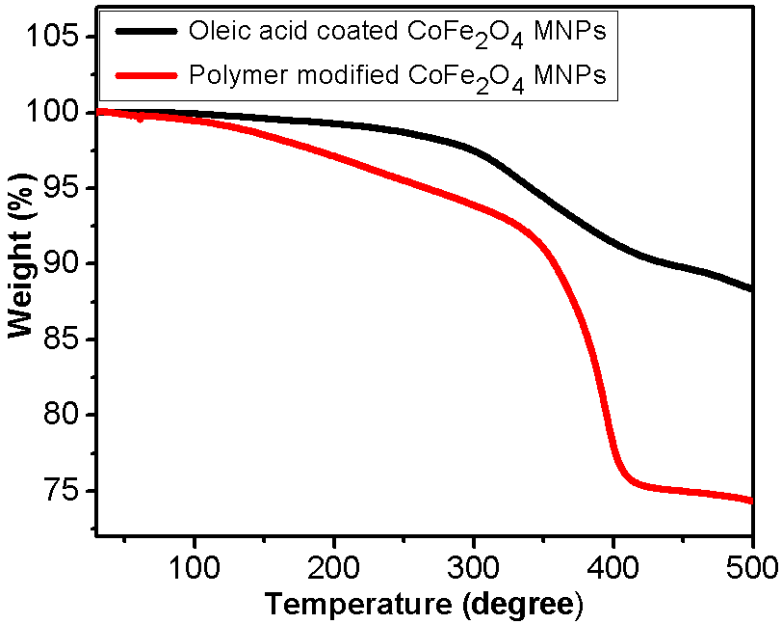

Figure S5. The room temperature hysteresis loop of $CoFe_2O_4$ FMNPs before and after polymer modification

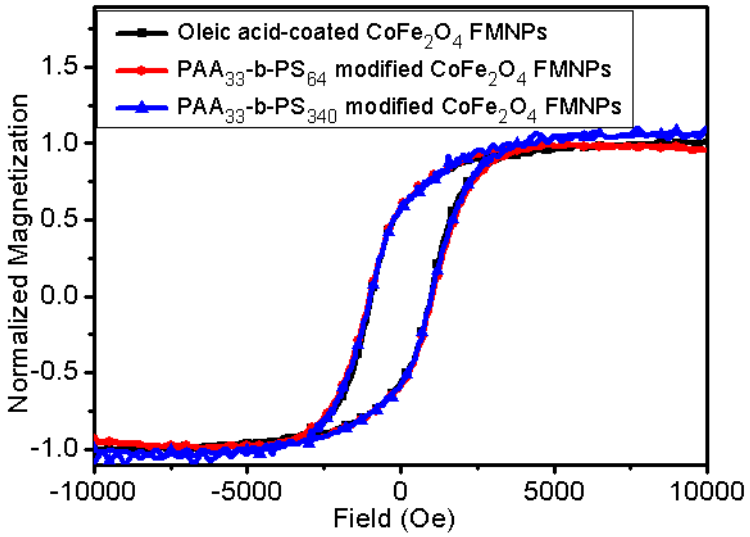

Figure S6. The Delta M curves of $CoFe_2O_4$ FMNPs before and after polymer modification

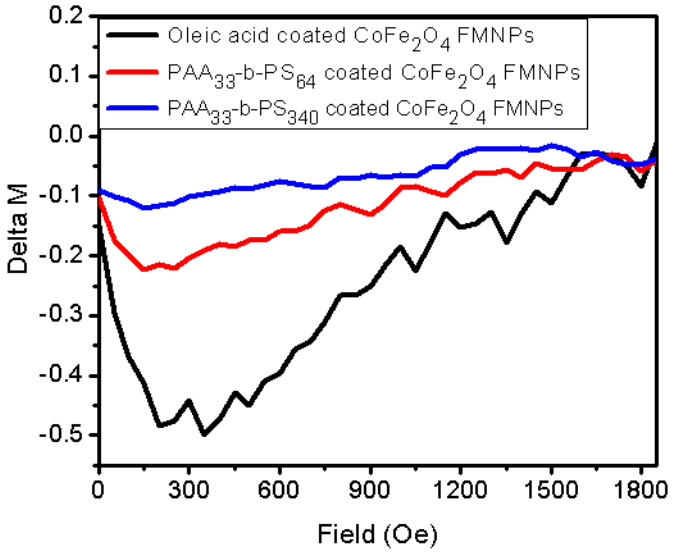

Figure S7. SEM top-down image of self-assembled PAA_{33}-b-PS_{340} block polymer-modified $CoFe_2O_4$ FMNP assemblies

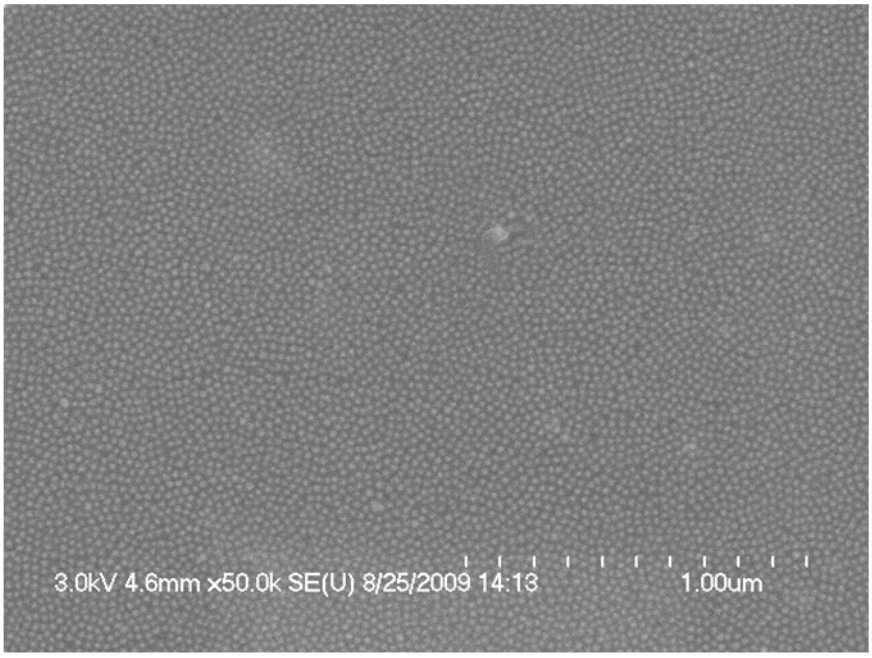

Figure S8. The SEM image of solvent evaporation-induced self assembly of $CoFe_2O_4$ FMNPs in the presence of magnetic field (5000 k Gauss)

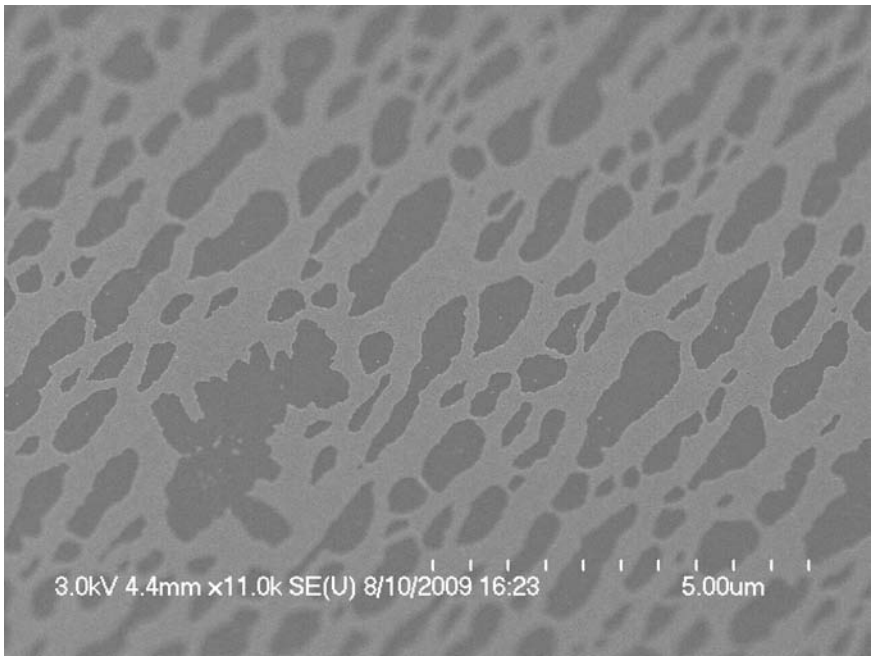

Figure S9. (a) TEM cross-section and (b) SEM top-down image of PAA_{33}-b-PS_{340} block copolymer-modified $CoFe_2O_4$ FMNP assemblies after magnetic alignment at 105°C

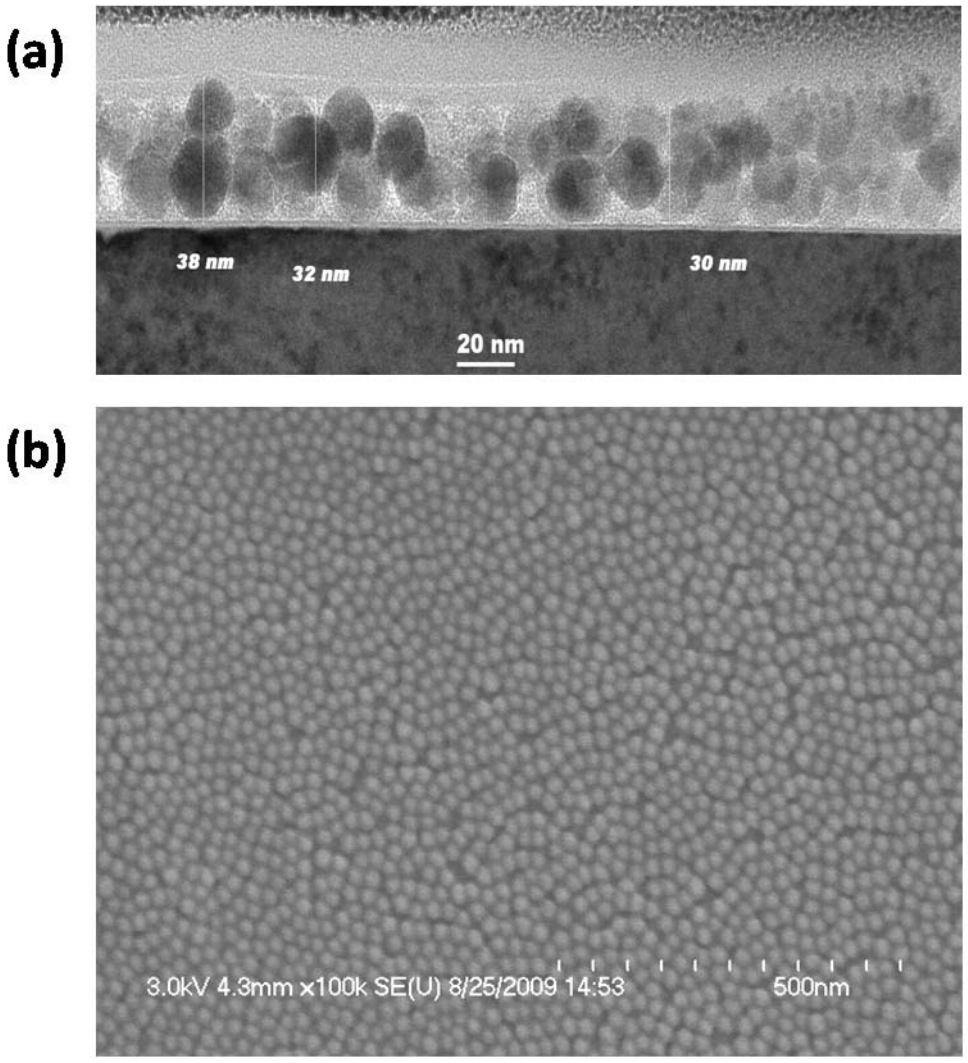

Figure S10. The write voltage dependence of the amplitude of 1 μm period signal

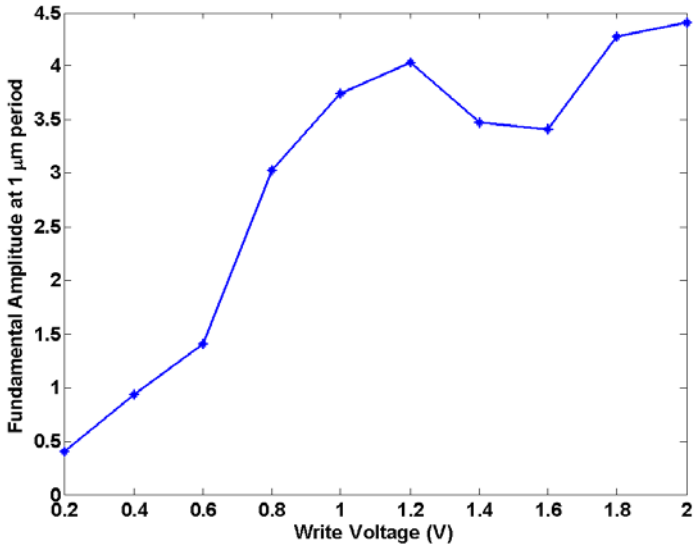

Figure S11. The readback signal from three tracks with spatial periods of 1 µm, 0.7 µm, and 0.4 µm