Supporting Information

The core-shell engineering on energy product of magnetic nanometals

Wei Zhang¹, Weibing Yang², Ravini U. Chandrasena², V. Burak Özdöl³, Jim Ciston³, Michael Kornecki⁴, SelvaVennila Raju⁴, Raymond Brennan⁴, Alexander X. Gray², and Shenqiang Ren^{1*}

1. Department of Mechanical and Aerospace Engineering, and Research and Education in Energy, Environment & Water (RENEW) Institute, University at Buffalo, The State University of New York, Buffalo, NY 14260

2. Department of Physics, Temple University, Philadelphia, Pennsylvania 19122, United States

3. National Center for Electron Microscopy Facility, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

4. U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States

*Correspondence should be addressed to: S. R. <u>shenren@buffalo.edu</u>

Experimental

Materials: Iron pentacarbonyl ($Fe(CO)_5$) and cobalt carbonyl ($Co_2(CO)_8$) were used as the precursors for synthesizing FeCo nanoparticles. All chemicals were purchased from Sigma-Aldrich and used as-received.

Synthesis of FePt-FeCo core-shell nanoparticles: The synthesis of FePt was described in a separate reference.¹ Platinum acetylacetonate (0.25 mmol), 1,2-hexadecanediol (0.75 mmol), and dioctylether (10 ml) were mixed in a three-neck-flask, vacuumed, and filled with argon three times, before heating to 373 K. Oleic acid (0.25 mmol), oleylamine (0.25 mmol), and Fe(CO)₅ (0.5 mmol) were added, and the mixture was heated to reflux (570 K). The refluxing step was continued for 30 minutes. The heat source was then removed, and the reaction mixture was allowed to cool to room temperature in order to obtain FePt-FeCo core-shell nanoparticles with various shell thicknesses. Different amounts of Fe(CO)₅ (from 0.05mmol to 3 mmol) and Co₂(CO)₈ (from 0.0083mmol to 0.5 mmol) were added into the reacted solution, heated to 433 K, and held for an additional 30 minutes (More detailed information provided in SI Table 1). Finally, the assynthesized nanoparticles were washed and calcined at 1023 K for 2 hours in an atmosphere of 5% H₂ balanced by N₂ to obtain the final product.

Characterization: The morphologies of the resultant samples were analyzed by scanning electron microscopy (SEM, FEI Quanta 450) and transmission electron microscopy (TEM, JEOL JEM-1400). High-resolution scanning transmission electron microscopy (STEM) measurements were carried out using the aberration-corrected TEAM I microscope at the National Center for Electron Microscopy Facility in the Molecular Foundry at Lawrence Berkeley National Laboratory. All geometric aberrations were corrected to the third order with a convergence semi-angle of 17 mrad and a collection semi-angle of 53-260 mrad. The structural properties were determined by Energy Dispersive Spectroscopy (EDS; FEI Quanta 450) and X-ray Diffraction (XRD) (Bruker D8 Discover). The magnetic properties were measured using a vibrating sample magnetometer (MicroSense EV7) with fields up to 21 kOe.

Reference

1. Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. science 2000, 287(5460), 1989-1992.



Figure S1 (a) SEM images of calined FePt nanowires at 1023 K for 2h, (b) The magnetic hysteresis loops of calcined FePt nanoparticles (black) and FePt nanowires (red) measured at room temperature, showing the synthesized FePt nanoparticle has a larger coercivity than that of the FePt nanowire.



Figure S2 Energy dispersive X-ray spectroscopy (EDS) spectra of FePt nanoparticles with different element ratios.



Figure S3 Transmission electron microscopy (TEM) images of as-prepared FePt-FeCo core-shell nanoparticles obtained by adding different molar ratios of FeCo precursors during the reaction. The molar ratios of FePt to FeCo are 12:1, 1:2, and 1:4, respectively (Figure a, b and c). These results indicate that the shell thickness of as-synthesized core-shell nanostructures could be tuned in this study and the related shell thicknesses are 1.1 ± 0.089 , 2.1 ± 0.148 and 2.8 ± 0.827 nm, respectively. All the shell thicknesses are measured in ImageJ, and 6 particles are randomly selected for each sample.



Figure S4 (a) SEM images of calcined FePt-FeCo nanoparticles at 1023 K for 2h, (b) Energy dispersive X-ray spectroscopy (EDS) spectra of FePt-FeCo nanoparticles. The existence of Co energy peaks indicates that the composite nanoparticle with constituent Fe, Pt and Co has been synthesized successfully.



Figure S5 Second-quadrant B-H curves for the FePt/FeCo nanoparticles with a shell thickness of ~0.9 nm after calcination at different temperatures for 2h.

Table 1 Various shell thickness of FePt-FeCo core-shell nanoparticles obtained by adding differentmolar ratios of FeCo precursors during the reaction.

FePt/FeCo	Fe(CO)5 (mmol)	Co ₂ (CO) ₈ (mmol)	Shell Thickness
			(nm)
15/1	0.05	0.0083	0.9±0.279
12/1	0.0625	0.0104	1.1±0.089
10/1	0.075	0.0125	1.2±0.374
1/2	1.5	0.25	2.1±0.148
1/3	2.25	0.375	2.4 <u>±</u> 0.481
1/4	3	0.5	2.8 <u>±</u> 0.827