Supporting Information (SI)

Effects of Mesoporous Silica Coating and Post-Synthetic Treatment on the Transverse Relaxivity of Iron Oxide Nanoparticles

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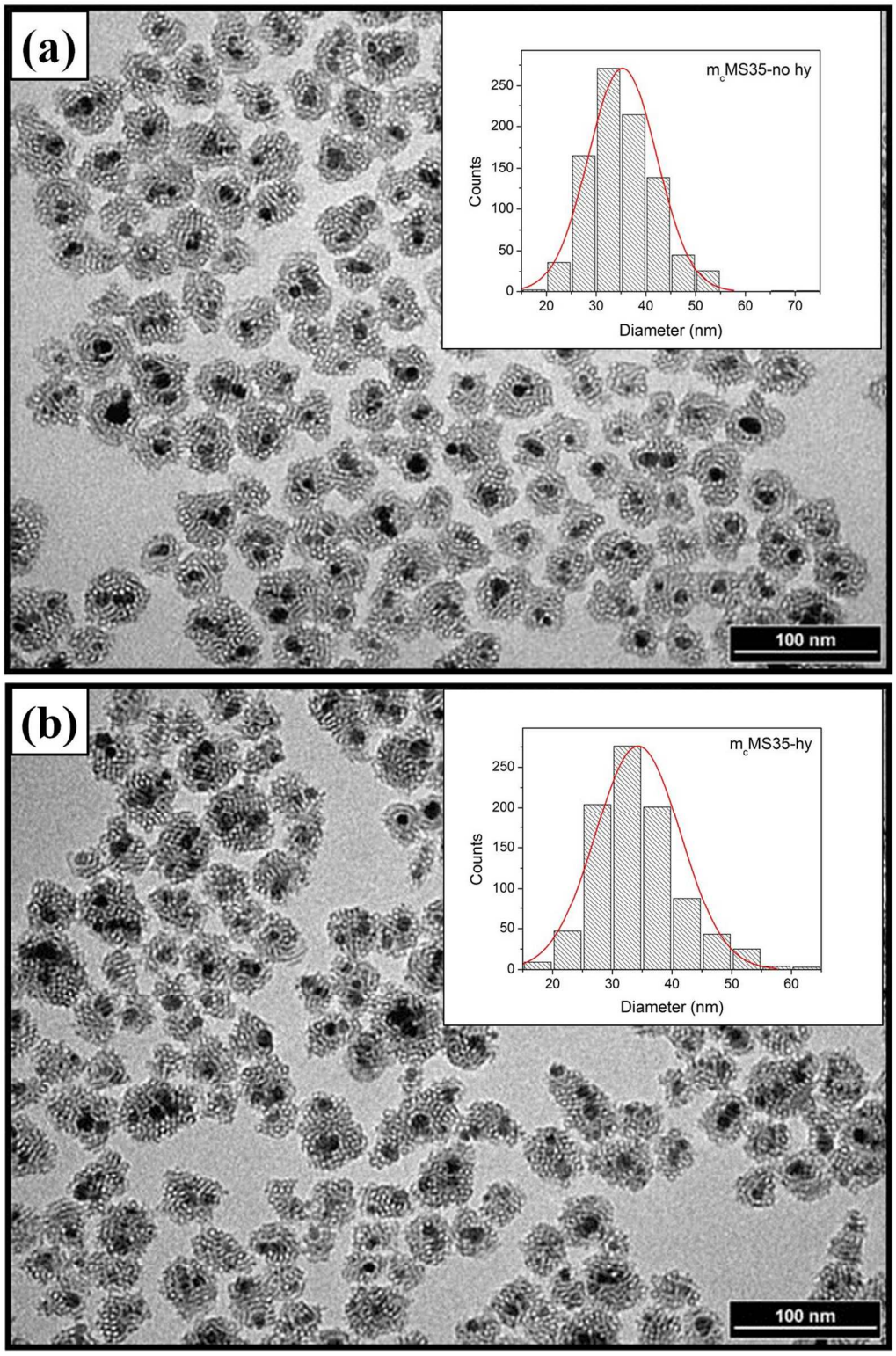
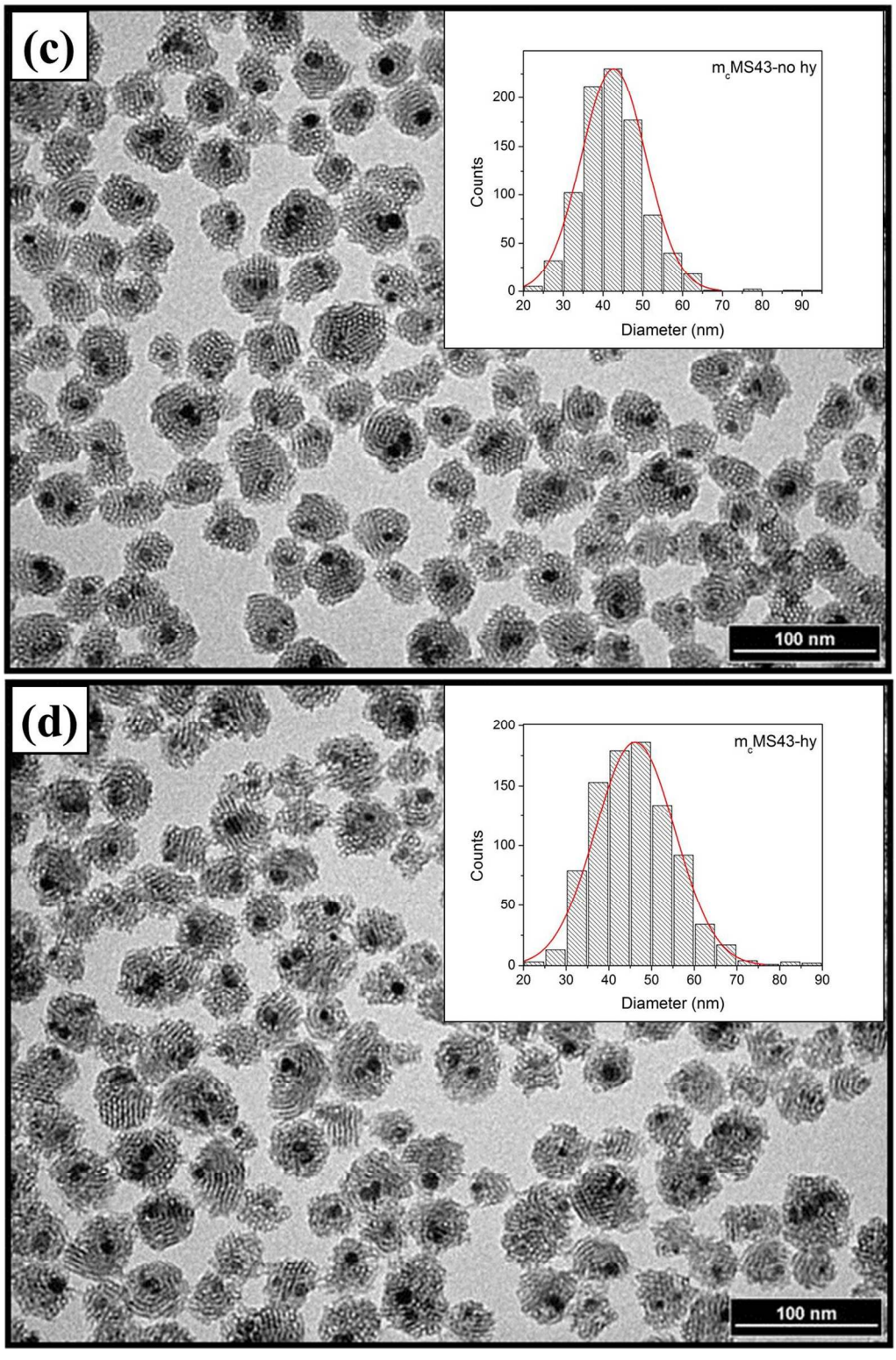
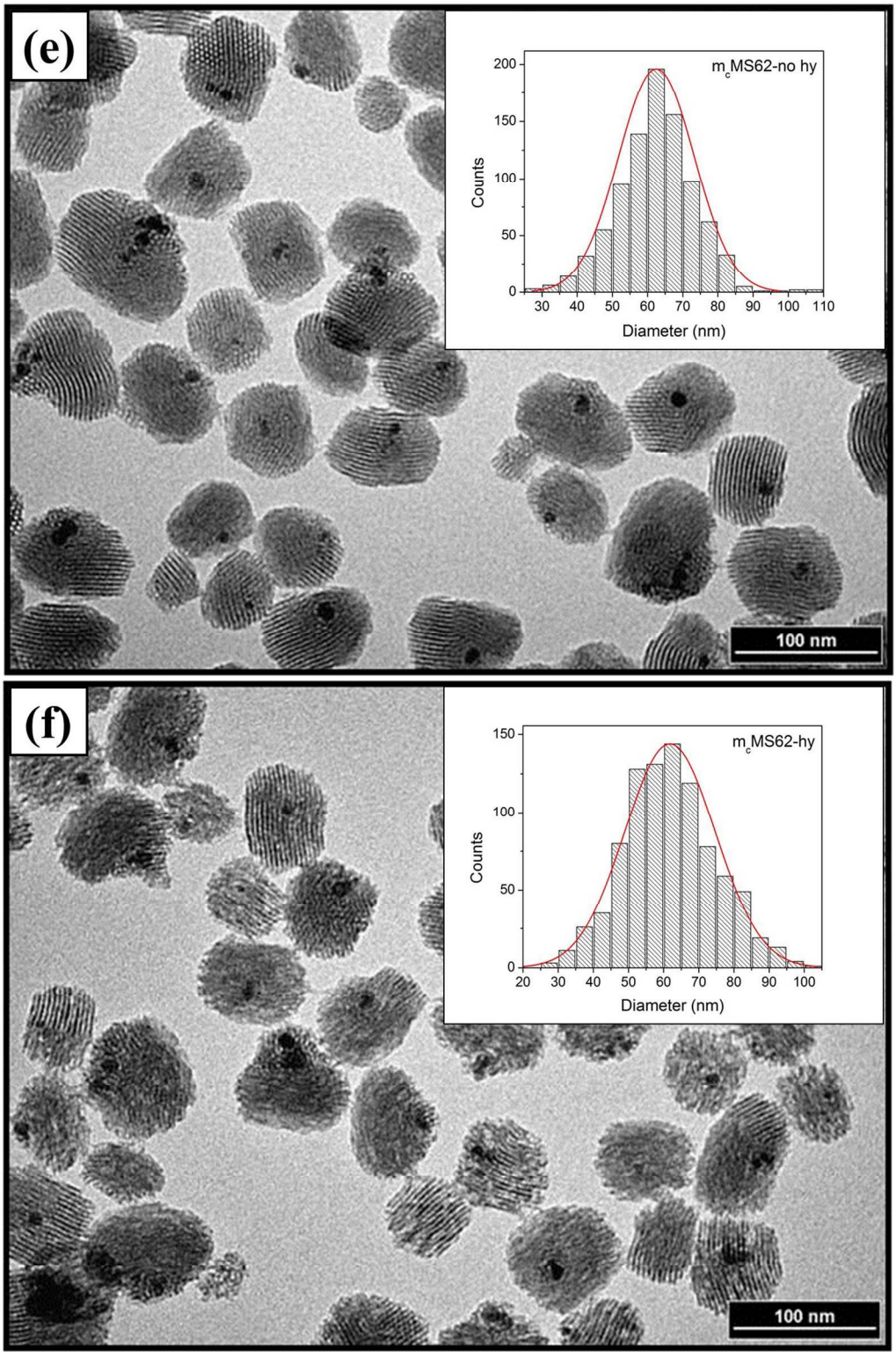
Table S1 EELS intensity data of m_dMS-62 after one and 14 days in water. Using a Digital Micrograph add-on, peak intensities either before or after background subtraction can be performed.[1] With any background condition, the L_3/L_2 ratio increases over 14 days.

Background		Day 1 Peak Intensity (e^-)	Day 1 Peak Range (eV)	Day 14 Peak Intensity (e^-)	Day 14 Peak Range (eV)
BG Included	L_3 intensity	75344	709.8 to 715.2	83717	710.1 to 715.8
	L_2 intensity	22353	722.4 to 727.8	21434	723.9 to 733.2
	L_3/L_2 ratio	3.37		3.91	
Pre-oxygen BG subtracted	L_3 intensity	75599	709.8 to 715.2	84044	710.1 to 715.8
	L_2 intensity	22587	722.4 to 727.8	21915	723.9 to 733.2
	L_3/L_2 ratio	3.35		3.83	
Pre-iron BG subtracted	L_3 intensity	75733	709.8 to 715.2	83404	710.3 to 716.0
	L_2 intensity	22696	722.4 to 727.8	21873	724.1 to 733.7
	L_3/L_2 ratio	3.34		3.81	


(a)
m_cMS35-no hy
Counts
Diameter (nm)
100 nm
(b)
m_cMS35-hy
Counts
Diameter (nm)
100 nm


(c)
m_cMS43-no hy
Counts
Diameter (nm)
100 nm
(d)
m_cMS43-hy
Counts
Diameter (nm)
100 nm


(e)
m_cMS62-no hy
Counts
Diameter (nm)
100 nm
(f)
m_cMS62-hy
Counts
Diameter (nm)
100 nm

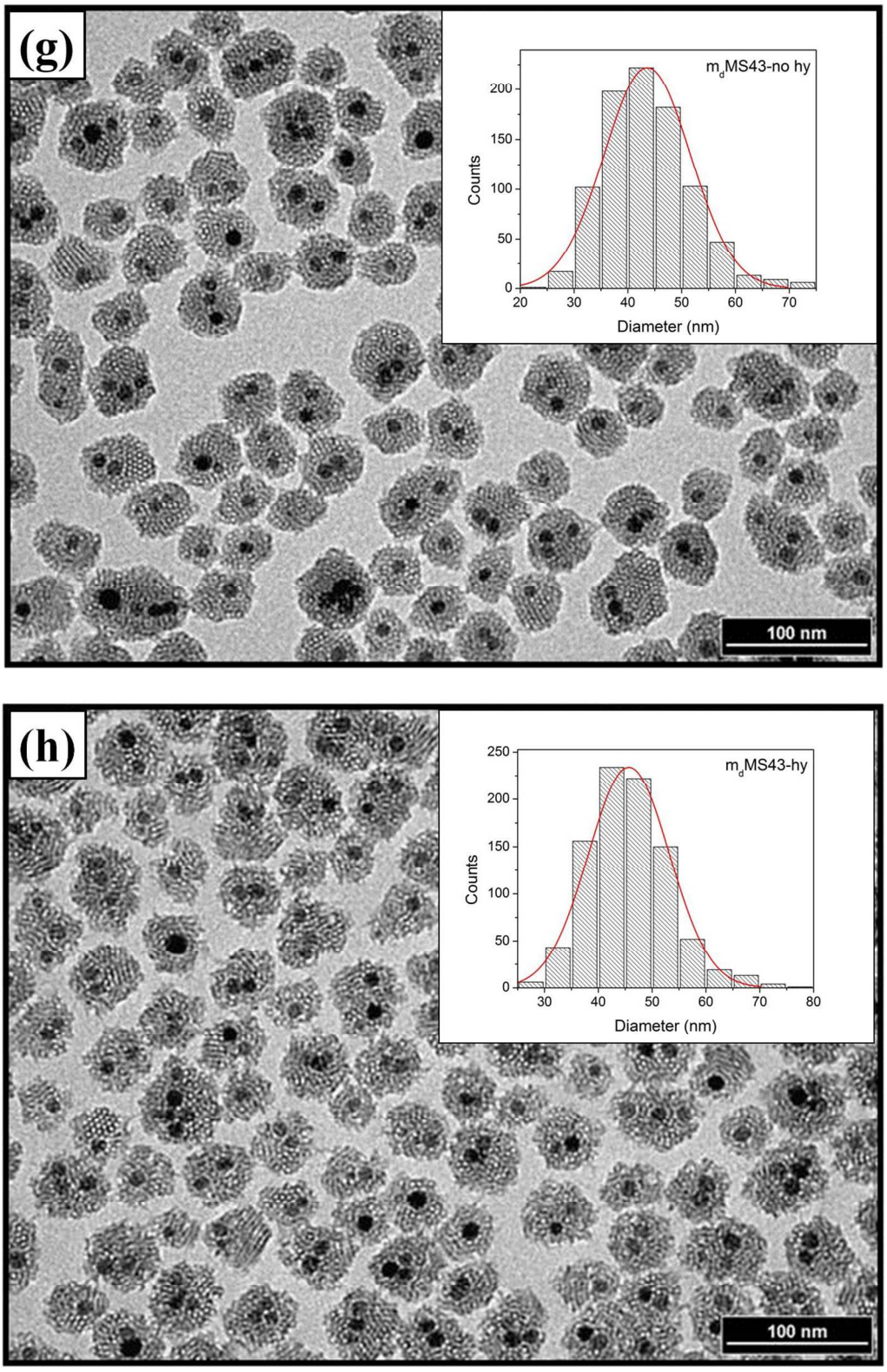


Figure S1. Enlarged TEM images of mMS NPs found in Figure 1 (a) through (h) with histograms for each condition (n=900).

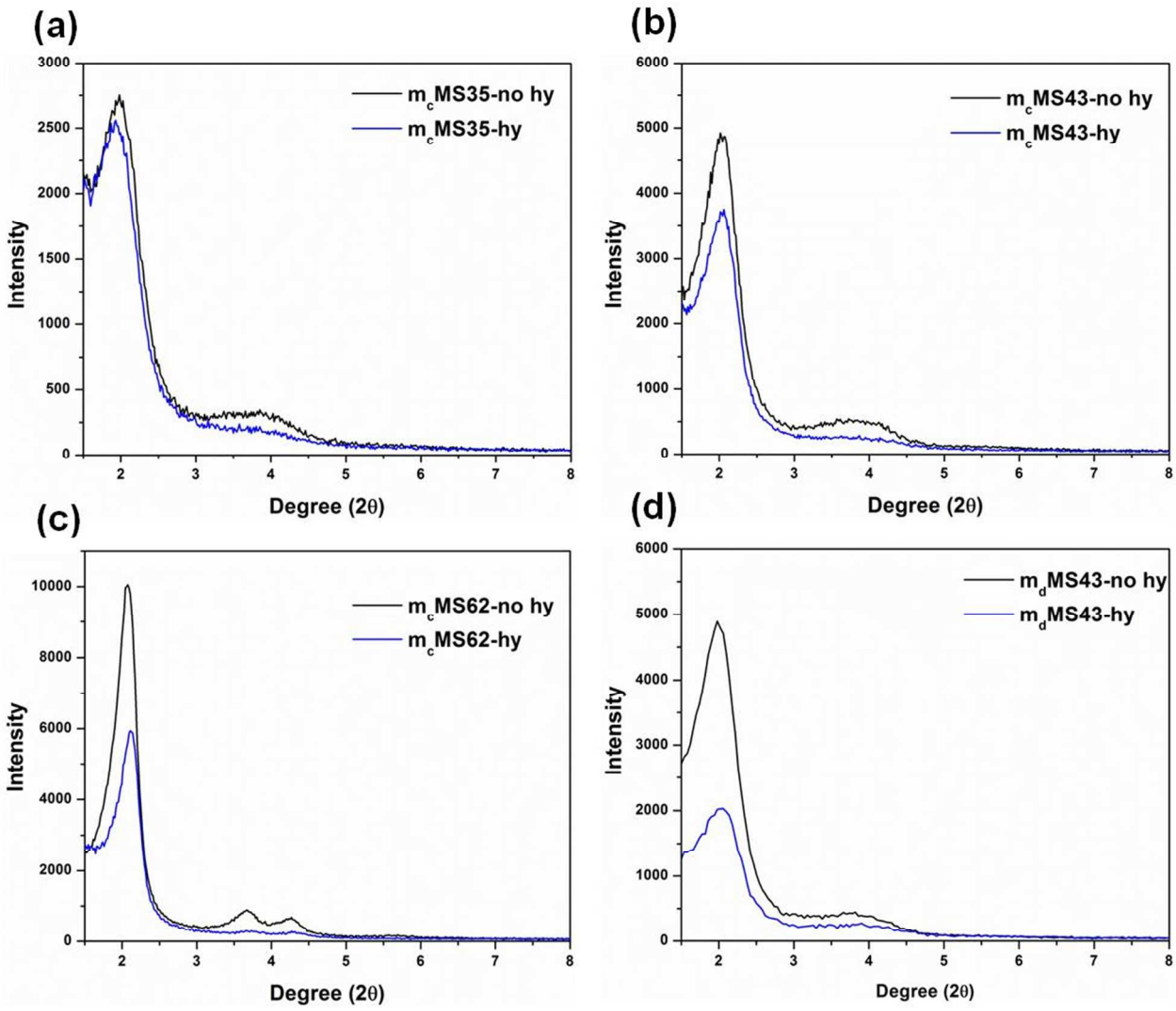


Figure S2. Low angle XRD showing 2D hexagonal pore ordering for different mMS NPs. Hydrothermally treated samples display broader peaks with lower intensity than those without hydrothermal treatment, consistent with previous work.[2,3] Larger overall nanoparticle diameters contribute to longer range 2D order and higher peak intensities. Differences in SPION core syntheses appear to have no effect on 2D pore ordering. (a) m_cMS-35 (b) m_cMS-43 (c) m_cMS-62 and (d) m_dMS-43.

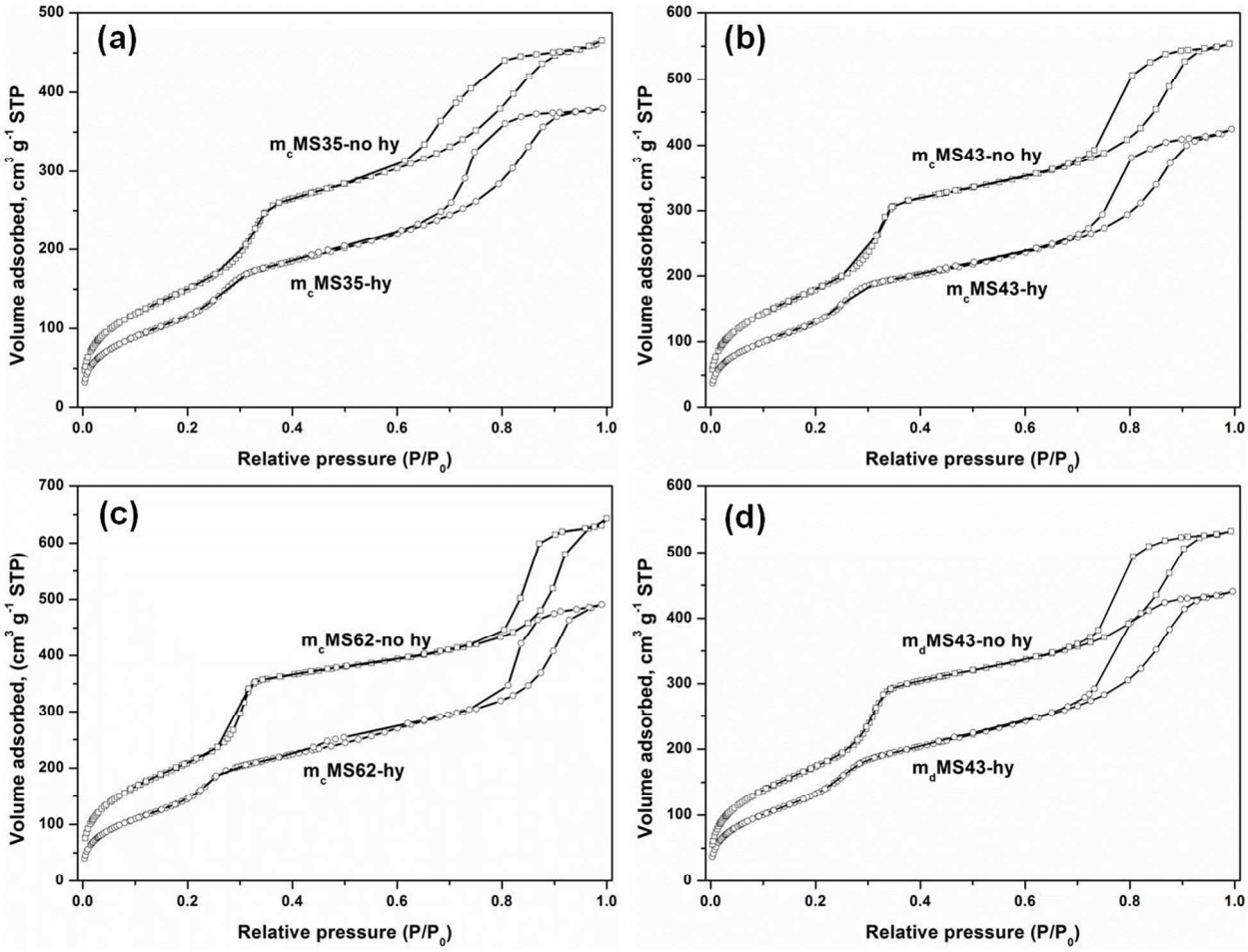


Figure S3. Nitrogen adsorption/desorption isotherms for various mMS NPs. All plots display type IV isotherms, indicating the presence of mesopores. Hydrothermally treated samples consistently display lower surface area and pore volume than those without hydrothermal treatment, likely due to more extensive incorporation of PEG-silane inside the pores.

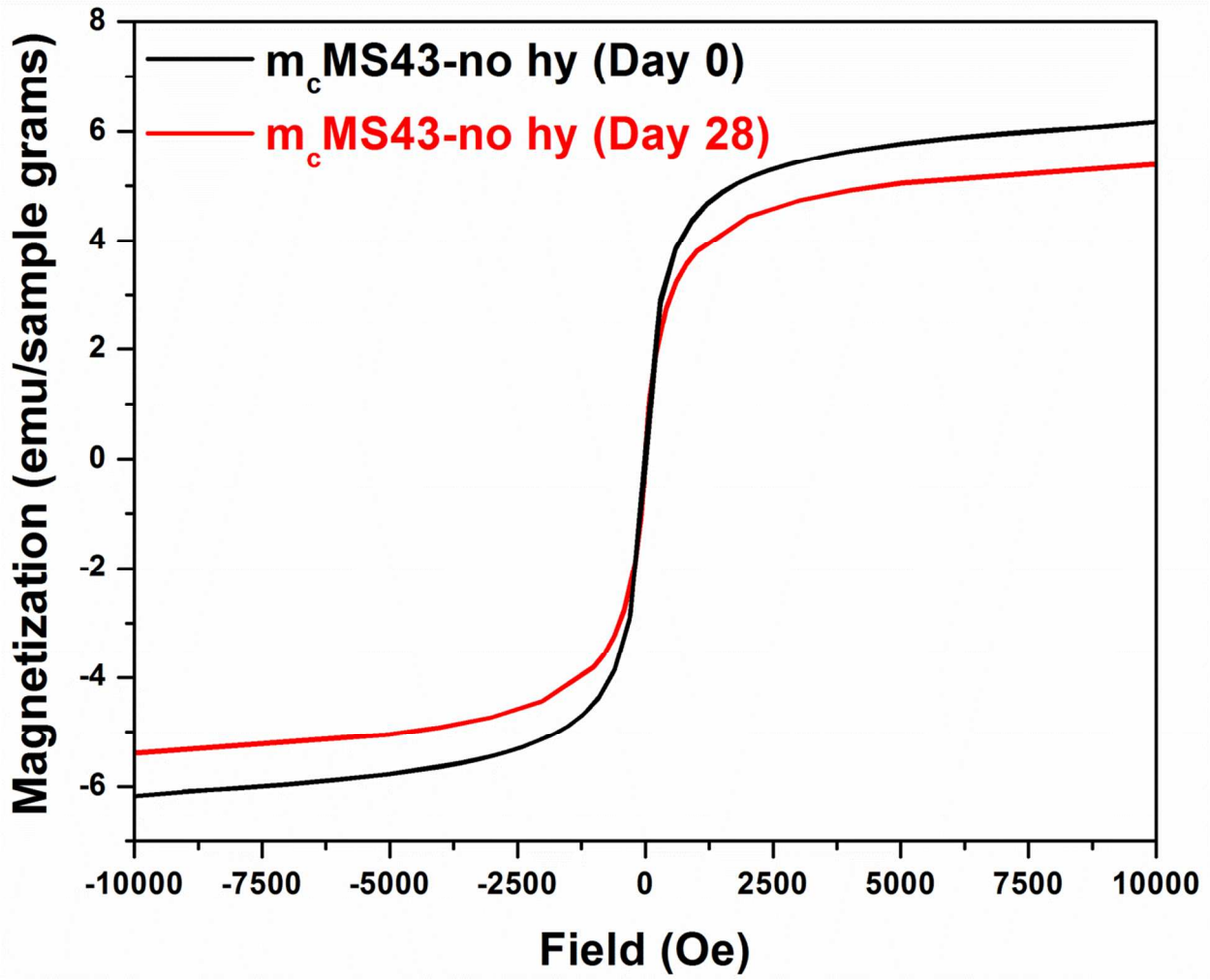


Figure S4. Room temperature magnetization curves of m_cMS43-no hy before and after 28-day storage measured by a Quantum Designs MPMS-5S cryogenic susceptometer.

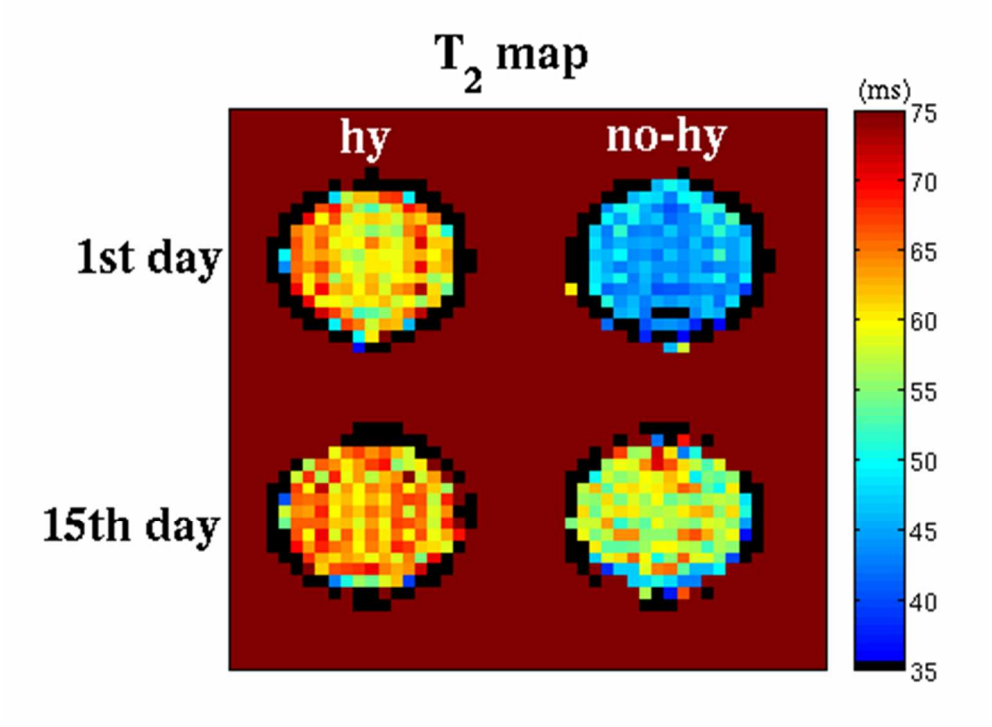


Figure S5. Color-scaled T_2 map collected for hy and no hy samples on day 1 and day 15 of aging in DI water. To determine mean T_2 values, data from 81 pixels were averaged for each sample.

Synthesis of SPIONs by decomposition of iron acetylacetonate ($Fe(acac)_3$)

Syntheses of decomposition SPIONs were performed according to literature procedures with small modifications.[4-5] Prior to synthesis, all reaction equipment (glassware, stir bars, etc.) was rinsed with a small amount of 12 M HCL and several portions of DI water. The equipment was dried in a drying oven or under a steady nitrogen flow. Once all the equipment was completely dry, 0.728 g of $Fe(acac)_3$ and 2.02 g of 1,2-dodecandiol were added to a 250 mL three neck round bottom flask and mixed with a spatula. Next, the flask was equipped with a reflux condenser and nitrogen flow, and 20 mL of benzyl ether were added to the flask. The solids were dissolved with intense stirring while the flask was kept under a flow of nitrogen. Once the solids were completely dissolved and the solution was a bright maroon color, 1.974 mL oleyl amine and 1.894 mL oleic acid were added. The flask was sealed under continuous nitrogen flow and heated in a sand bath to 200 °C at roughly 3 °C/min. We found that longer periods of time at both 200 and 300 °C allowed formation of more monodisperse particles, so the reaction was allowed to heat at 200 °C for 3 h before being heated to 300 °C at the same rate of 3 °C/min. While heating to 300 °C, the nitrogen flow was turned off to create a blanket of nitrogen over the liquid surface. Once at 300 °C, the suspension bubbled vigorously for about 30 min. Around this time, a series of violent reactions occurred during which the temperature would drop drastically (sometimes all the way to 220°C) and rise back to 290 °C within a few minutes. Following these reactions, it was very difficult to achieve temperatures of 300°C, but the suspension was kept between 285 and 300 °C for another 2 hours (2.5 h total). The reaction was removed from the sand bath and allowed to cool to room temperature with vigorous stirring and nitrogen flow. Once cool, workup proceeded as described in literature.[4,5] Seeded growth was

accomplished in the same way using 80 mg of seed NPs with longer reaction times (3 h and 2.5 h at 200 and 300 °C, respectively).

References:

1. Mitchell, D. R. G.; Schaffer, B. *Ultramicroscopy* **2005**, *103*, 319.

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4. Sun, S.; Zeng, H.; Robinson, D.B.; Raoux, S.; Rice, P.M.; Want, S.X.; Li, G. *J. Am. Chem. Soc.* **2004**, *126*, 273.

5. Sun, S.; Zeng, H. *J. Am. Chem. Soc.* **2002**, *124*, 8204.