Supporting information

List of abbreviations

pSi	Porous silicon
ET	Electron tomography
TEM	Transmission electron microscope
WBP	Weighted backprojection
SIRT	Simultaneous iterative reconstruction technique
ITK	Insight toolkit
DM	Digital micrograph
HAADF	High-angle annular dark field
LC	Local curvature
DF	Demagnetizing factor
MC	Monte carlo
ZFC	Zero field cooling
FC	Field cooling
SEM	Scanning electron microscope
FIB	Focused ion beam
FTIR	Fourier transform infrared
EDX	Energy dispersive X-ray
SQUID	Superconducting quantum interference device
VSM	Vibrating sample magnetometer
PRC	Projection-re-projection comparison
MSE	Mean squared error
MWC	Missing wedge correction

List of symbols

Z	Atomic number
T	Temperature
κ_1, κ_2	Maximum and minimum principal curvature
S	Shape index
r_S	Submerging ratio
A_O, A_I	Area outside and inside the template
T_B	Blocking temperature
K_μ	Anisotropy energy density
V	Volume
k_B	Boltzmann constant
μ_0	Permeability constant
M_S	Saturation magnetization
H_C	Coercive field
H	Magnetic field
K_{shape}	Anisotropy constant (shape)
N_a, N_b, N_c	Demagnetizing factors

A skeletonization of the data produces a so called centerline tree from the segmentation of the pores only. A Euclidian distance is calculated to the nearest boundary and stored in the graph as a thickness attribute as seen in figure 1. A visual investigation of this graph showed that the main pores were found to be separated as claimed in [1].

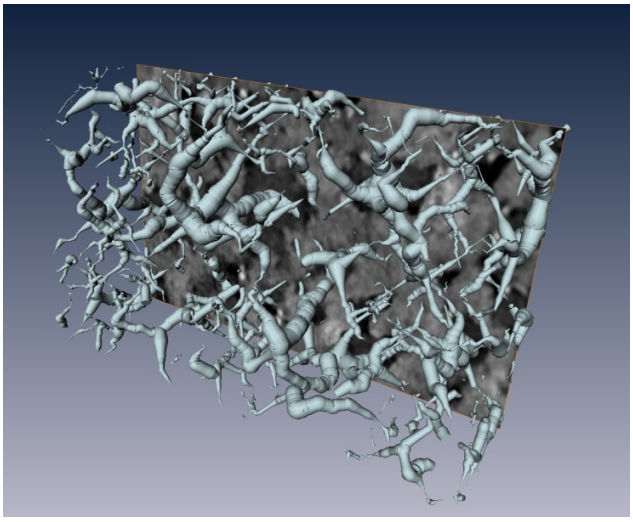

Fig. 1. A centerline tree graph of the pores in the reconstruction. The thick curves show the path of the main pores and the thinner ones the dendritic pores.

To prove that the polyfit method can adequately fit high curvature locations, a test image was created with a shape index value of 0.94 as seen in figure 2(a). A particle was placed within the high curvature location (figure 2(b)) and a clear change in the local curvature can be seen in the immediate proximity of the particle within the template surface.

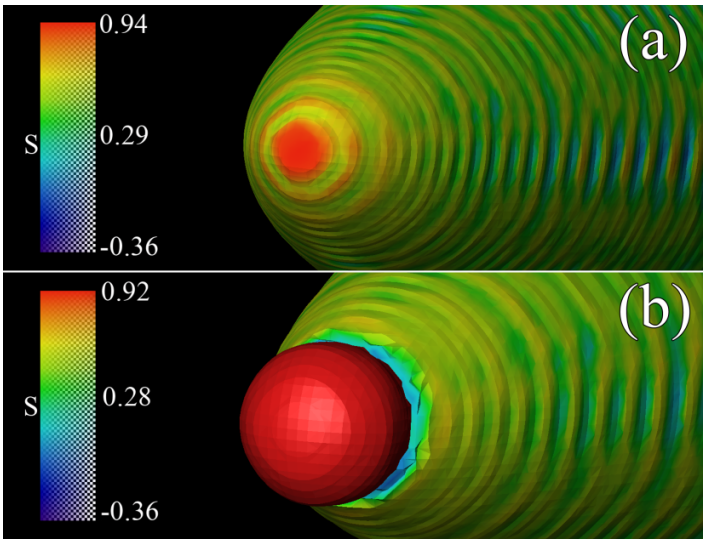

Fig. 2. (a) A test image with a high curvature location. (b) An adsorbed particle. The color bars represent the shape index value.

The acquired shape index using the ring method was 0.35, 0.4 and 0.5 for the rings 1, 3 and 5 respectively. A value of 0.99 was obtained using the mean coordinates of the fitted surface inside the particle area (one point only). Alternatively, when taking the mean shape index value of a small patch of points (as was done in the manuscript), i.e. points that are within a Euclidian distance of 0.5 to the mean value of the fitted point coordinates, a value of 0.96 was achieved.

The equations for the DFs of a general ellipsoid was solved by J. A. Osborn already in 1945 and are defined as [2]

$$N_a = 4\pi \frac{\cos\varphi \cos\vartheta}{sin^3\vartheta\ sin^2\alpha} [F(k,\vartheta) - E(k,\vartheta)], \quad (1)$$

$$N_b = 4\pi \frac{\cos\varphi \cos\vartheta}{sin^3\vartheta\ sin^2\alpha\ cos^2\alpha} \left[E(k,\vartheta) - cos^2\alpha\ F(k,\vartheta) - \frac{sin^2\alpha \sin\vartheta \cos\vartheta}{cos\varphi} \right] \quad (2)$$

and

$$N_c = 4\pi \frac{\cos\varphi \cos\vartheta}{sin^3\vartheta\ cos^2\alpha} \left[\frac{\sin\vartheta \cos\varphi}{\cos\vartheta} - E(k,\vartheta) \right], \quad (3)$$

where N_a, N_b and N_c are the DFs corresponding to the ellipsoid's semi axes a, b and c with $a \geq b \geq c \geq 0$. F( ) and E( ) are elliptic integrals of first and second kinds respectively. Also

$\cos\vartheta = c / a$, where $(0 \leq \vartheta \leq \pi/2)$,

$\cos\varphi = b / a$, where $(0 \leq \varphi \leq \pi/2)$ and

$\sin\alpha = \sin\varphi / \sin\vartheta = k$, where $(0 \leq \alpha \leq \pi/2)$.

These equations can be directly used with the values a, b and c, that can be acquired from the ellipsoidal fit of the nanoparticles.

To model the assembly of the nanoparticles with Monte Carlo method we consider N_p magnetic particles (grains), with ellipsoidal shape. The magnetic particles are single-domain and each of them is represented by a three-dimensional classical spin [3] with magnetic moment $\vec{m}_i = m_i\vec{s}_i,\ i = 1, \ldots, N_p$ of magnitude $m_i = M_S V_i$ and direction $\vec{s}_i$, with $|\vec{s}_i| = 1$, where M_s is the saturation magnetization per unit volume and V_i is the particle volume. From the quantitative analysis of the reconstructed volume, N_p = 1042 particles were extracted, along with the knowledge of the particle positions (x_i,y_i,z_i), the particle dimensions

(the lengths of the three semi-axis a_i, b_i, c_i of the ellipsoid), the particle volume and surface area, the 3 unit vectors along the principal axis of the fitted ellipsoid representing the particle $\hat{a} = (a_x, a_y, a_z)$, $\hat{b} = (b_x, b_y, b_z)$ and $\hat{c} = (c_x, c_y, c_z)$ where a-axis is the major axis and c-axis is the minor axis. The demagnetizing tensor $\mathbf{N}_i$ has eigenvalues N_a, N_b, N_c along the principal axis of the ellipsoid. We have estimated that the metal volume fraction of the assembly is $x_V \sim 0.04$ (concentration ~ 20 mg/ml) so we can assume that the particles do not touch each other and there is no direct exchange interaction between them. The nanoparticles interact only via long-range dipolar forces.

A uniaxial easy axis $\hat{e}$ was assigned to each particle and the easy axes of the nanoparticles in the assembly were randomly distributed. The nanoparticles anisotropy includes contributions from the crystallographic and surface anisotropy. Ellipsoidal nanoparticles have also shape anisotropy, which usually is included in an effective anisotropy constant. In our case, due to the detailed knowledge of the particle morphology, the shape anisotropy was taken into account in our model explicitly, through the DF's. The demagnetizing field of the i-th particle is $H = -M_S \mathbf{N}_i \vec{s}_i$ and the respective self-energy of the nanoparticle is $E_{d,i} = \frac{1}{2}\mu_0 M_S V_i^2 \vec{s}_i N_i \vec{s}_i$. The energy of the assembly is

$$E = -\mu_0 H M_S \sum_{i=1}^{N} V_i \vec{s}_i \hat{e}_h - K_\mu \sum_{i=1}^{N} V_i (\vec{s}_i \hat{e}_i)^2 - \frac{1}{2}\frac{\mu_0 M_S^2}{4\pi a^3} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} V_i V_j \vec{s}_i \mathbf{D}_{ij} \vec{s}_j + \frac{1}{2}\mu_0 M_S^2 \sum_{i=1}^{N} V_i (\vec{s}_i \mathbf{N}_i \vec{s}_i), \quad (4)$$

where μ_0 is the permeability constant, $\widehat{e}_h$ and $\widehat{e}_i$ are the directions of the magnetic field and the anisotropy axis of the i-th particle, $\mathbf{D}$ is the Dipole –Dipole interaction tensor $\mathbf{D}_{ij} = \frac{3\hat{r}_{ij}\hat{r}_{ij} - 1}{r_{ij}^3}$ where i ≠ j, $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and $\hat{r}_{ij} = \vec{r}_{ij}/r_{ij}$, are the interparticle distance and the direction vector joining the sites i and j respectively, measured in units of the characteristic length **a**. When particles are placed on a lattice structure, **a** is usually taken to be the lattice constant, but in our case it was taken to be 1 nm.

In the case of polydisperse assemblies we define the mean particle volume $\langle V \rangle = \sum_{i=1}^{N_p} V_i / N_p$ and using the dimensionless magnetic moments $n_i = V_i / \langle V \rangle$ we express the magnitude of the magnetic moment as $m_i = M_S V_i = (M_S \langle V \rangle) n_i$. We rescale all energy terms by dividing with the mean anisotropy $K_\mu \langle V \rangle$ per particle, so we use in the calculations the reduced (dimensionless) parameters

$$h = \mu_0 \frac{M_S}{K_\mu} H, \qquad k = 1, \qquad g = \frac{\mu_0 M_S^2 \langle V \rangle}{4\pi K_\mu a^3} \text{ and } d = \frac{\mu_0 M_S^2}{2K_\mu} \tag{5}$$

for the external magnetic field *h*, the nanoparticle anisotropies *k*, the DDI strength *g* and the demagnetizing energy parameter d respectively. Then the reduced energy is written as

$$\varepsilon = \frac{E}{K_1 \langle V \rangle} = -h \sum_{i=1}^{N} n_i \vec{s}_i \hat{e}_h \; - \; k \sum_{i=1}^{N} n_i (\vec{s}_i \hat{e}_i)^2 - \frac{1}{2} g \sum_{\substack{i,j=1 \\ i \neq j}}^{N} n_i n_j \left(\vec{s}_i \mathbf{D}_{ij} \vec{s}_j \right) + \frac{1}{2} d \sum_{i=1}^{N} n_i (\vec{s}_i \mathbf{N}_i \vec{s}_i) \tag{6}$$

and the thermal energy is $\mathrm{t_K} = \mathrm{k_B}/\mathrm{K_\mu}\langle \mathrm{V} \rangle$ and $\mathrm{t} = \mathrm{t_K T}$.

References

1. Granitzer, P.; Rumpf, K.; Venkatesan, M.; Roca, A. G.; Cabrera, L.; Morales, M. P.; Poelt, P.; Albu, M *J. Electrochem. Soc., 157 (7) K145-K151,* **2010**

2. Osborn, J. A. *Phys. rev.,* vol. 67, no. 11 and 12, pp. 351-357, **1945.**

3. Coey, J. M. D. *Magnetism and Magnetic Materials,* New York, **2010.**