Supplementary information

Microfluidic-based synthesis of non-spherical magnetic hydrogel microparticles

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Contents:

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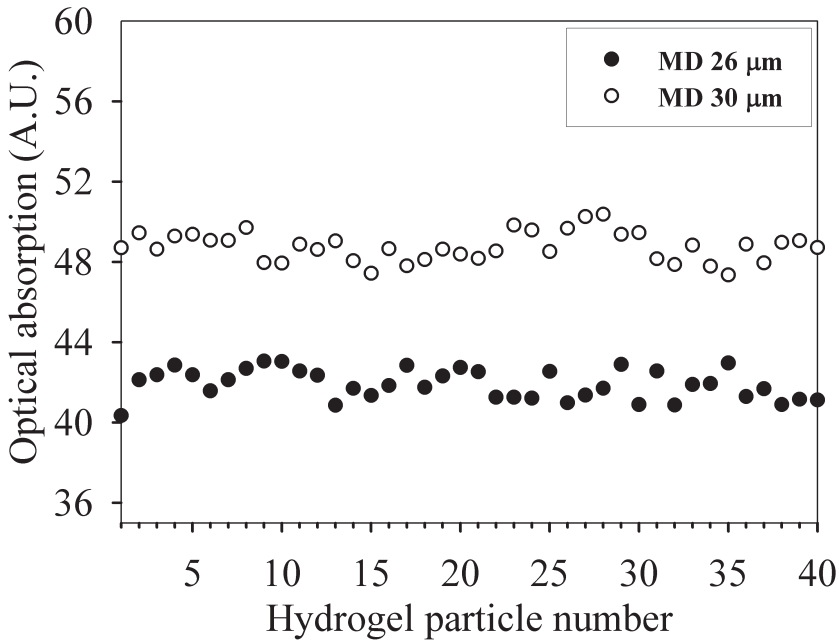

Figure S1: Optical absorption of spherical magnetic hydrogel particles with mean diameters (MD) of $26\mu m$ and $30\mu m$. Each symbol represents an individual particle. Adsorption CVs are 1.8% and 1.5% for the $26\mu m$ and $30\mu m$ hydrogel particles respectively. We first obtained the luminosity from a fixed area selected on a magnetic hydrogel particle and repeated the measurement for the other particles. The measured luminosity of the magnetic hydrogel particles were then corrected by subtracting the background.

Magnetic properties of spherical microparticles

Table S1 shows sample data from other studies for magnetic microparticles synthesized using batch polymerization methods. The last two entries in the table are for commercially available microparticles. Magnetic properties of the microparticles (e.g. magnetic susceptibility and saturation) depend strongly on the nature of physically encapsulated magnetic nanoparticles into the polymer matrix. The magnetization of the nanoparticles are greatly influenced by multiple complex factors such as their chemical composition, size, degree of crystallization, inter-particle interactions [6–10] and thus the synthesis process used. Microparticles synthesized using the same batch of magnetic nanoparticles will have a M_{so} that increases approximately linearly with weight % of magnetic nanoparticles. This trend is clearly seen in the data by Fonnum et al. [5]. The value of M_{so} we attain for our microhydrogel particles is similar to that found for the commercially available COMPEL$^{\mathrm{TM}}$ particles which contain a similar loading of magnetic material.

At small field strengths, the magnetization of the microparticles increases linearly with the applied field and the coefficient of proportionality is the magnetic susceptibility χ_{dry}.

Table S1: Typical magnetic properties of spherical microparticles (MP) produced by other methods. All data is for dried samples except for that of Menager et al. [1].

	Nano particle	Host polymer	Diameter of MP (μm)	CV of MP diameter (%)	Nanoparticle content wt (%)	χ_{dry} (m^3/kg)	M_{so} (Am^2/kg)
Menager et al. [1]	γ-Fe_2O_3	AM/MBA	10−60[a]	–	64/34[b]	–	–
Zhang et al. [2]	Fe_3O_4	Chitosan	150−400[a]	–	–	6.28×10^{-5}	4.11
Deniz & Amet [3]	Fe_3O_4	Mowital	125−250[a]	–	–	5.34×10^{-5}	4.7
Xie et al. [4]	Fe_3O_4	PLGA(40KDa) PLGA(5KDa) PLA−PEG	21±8 8±3 53	–	11.5−14.5	–	6.9−8.7
Fonnum et al. [5]	γ-Fe_2O_3 & Fe_3O_4	PS	4.40[c] /2.83[d]	1.2 /1.4	20.2 /11.8	102×10^{-5} /54×10^{-5}	19.6 /10.8
COMPEL[TM,e]	Fe_3O_4	proprietary	8	≤ 5	2.4−3.8	13.8×10^{-5}	2.54

[a] Magnetic microparticle diameters vary in the indicated range.
[b] Two different iron contents depending on two weight ratios (5wt% and 2.5wt% MBA/AM).
[c] Dynabead product: M−45
[d] Dynabead product: M−280
[e] Information supplied by the manufacturer, Bangs Laboratories, Inc.
PS Polystyrene AM Acrylamide MBA N,N'-methylenebisacrylamide PLGA Poly(D,L-lactide)-co-glycolide
PLA-PEG Poly(D,L-lactide)-co-poly(ethylene glycol) Mowital MowitalB30HH(polyvinylbutyral)

Most of the microbeads in Table S1 have values of χ_{dry} which are very similar to our sample, except for the beads studied by Fonnum et al. [5]. To gain insight into these trends we present a simple formula for the predicted susceptibility (neglecting the surrounding medium susceptibility, remnant magnetization and any nonmagnetic material on the nanoparticles) [11]:

$$\chi_{dry} = \frac{\pi}{18}\phi\mu_o\frac{M_s^2 d^3}{\rho_{nano}k_bT}, \tag{1}$$

where μ_o is the permeability of vacuum, d is the nanoparticle diameter, ϕ is the weight fraction of magnetic particles, and ρ_{nano} is the density of the pure magnetic material. This relation shows the strong dependence of χ_{dry} on both the nanoparticle size (d) and extent of loading (ϕ) in the microparticle. The microparticles studied by Fonnum et al. [5] again have a larger χ_{dry} mostly due to the larger loading of magnetic material and for their data $\chi_{dry} \sim \phi$.

References

[1] C. Menager, O. Sandre, J. Mangili, and V. Cabuil, *Polymer*, 2004, **45**, 2475–2481.

[2] J. Zhang, S. Zhang, Y. Wang, and J. Zeng, *J. Magn. Magn. Mater.*, 2007, **309**, 197–201.

[3] T. Deniz and A. R. Ozdural, *React. Funct. Polym.*, 2000, **43**, 279–286.

[4] Y. Xie, M. D. Kaminski, M. D. Torno, M. R. Finck, X. Liu, and A. J. Rosengart, *J. Magn. Magn. Mater.*, 2007, **311**, 376–378.

[5] G. Fonnum, C. Johansson, A. Molteberg, S. Morup, and E. Aksnes, *J. Magn. Magn. Mater.*, 2005, **293**, 41–47.

[6] A. Millan, A. Urtizberea, N. J. O. Silva, F. Palacio, V. S. Amaral, E. Snoeck, and V. Serin, *J. Magn. Magn. Mater.*, 2007, **312**, L5–L9.

[7] J. C. Bacri, R. Perzynski, D. Salin, V. Cabuil, and R. Massart, *J. Magn. Magn. Mater.*, 1986, **62**, 36–46.

[8] N. Feltin and M. P. Pileni, *Langmuir*, 1997, **13**, 3927–3933.

[9] C. J. Serna, F. Bodker, S. Morup, M. P. Morales, F. Sandiumenge, and S. Veintemillas-Verdaguer, *Solid State Commun.*, 2001, **118**, 437–440.

[10] Z. Shan, W. S. Yang, X. Zhang, Q. M. Huang, and H. Ye, *J. Braz. Chem. Soc.*, 2007, **18**, 1329–1335.

[11] R. E. Rosensweig, *Ferrohydrodynamics*, Cambridge University Press, New York, 1985.