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Kinetics of aggregation and magnetic separation of multicore iron oxide nanoparticles: effect of the grafted layer thickness

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Abstract: Magnetic microbeads are commonly used in immunoassays to detect trace levels of antigens. Despite weaker magnetic attraction, we aim at developing efficient magnetic capture of multi-core magnetic nanoparticles (MNP) also called nanoflowers,^[1] of outer diameter 30-60 nm, by using moderate magnetic field strengths. Recent work by some of us showed that magnetic interactions between MNPs of this size can still be strong enough to induce a reversible phase separation in the presence of a magnetic field B as weak as 10 mT.^[2] During this phase separation, MNPs are gathered into micron-sized drop-like aggregates whose magnetic interaction with the applied field is much stronger than between individual nanoparticles and larger than thermal agitation $k_B T$. These fluid-like aggregates can then be separated from the solvent much more easily than single MNPs. Moreover, it is beneficial in continuous filtration to assemble the aggregates well before they are captured by magnetized collectors, by conveying the MNP suspension to the micro-filter across a microchannel submitted to a uniform external magnetic field H_0 . This communication establishes the mechanisms of multi-core MNP capture in microfluidic channels under magnetic and flow fields, and presents a phase diagram in terms of Mason number, dipolar coupling constant, and thickness of the organic coating wrapping the multi-core MNPs: short citrate molecules or PEG chains.^[3,4]

Keywords: Multi-core magnetic Nanoparticles, Magnetic attraction, Micropillars, Microfluidics.

ImmunoMag project (funded by UCA^{JEDI} IdEx)

Microfluidic chip with magnetic micro-pillar to pre-concentrate MNPs

Capture of antigens by Ab grafted on MNPs and detection by secondary Ab

Magnetic beads at volume fraction ϕ_p incubated with target antigens ($C_{AG}^{(i)}$) and detection antibodies

Principle stages of microfabrication of a microfluidic channel for magnetic separation (a-f). (g): sketch of the microfluidic channel. (h): deposits of IONPs around the micropillar (deposit surface area S is hatched)

MNP synthesis in polyols (Fe_3O_4) and oxidation ($\gamma-Fe_2O_3$)

Poly(hydroxy) amine/Polyol viz. N-methyl diethanolamine / DEG (1:1)

- 6 mmol $FeCl_2$
- 12 mmol $FeCl_3$
- 180g DEG
- 180g NMEDEA
- 220°C 5h

FeCl₂·4H₂O/FeCl₃·6H₂O/NaOH (1/2/8)
Stoichiometric amount of water needed

Volume size distribution of multicore iron oxide nanoparticles (IONPs) measured by DLS and TEM (triangles). The hydrodynamic size distribution was measured by DLS on IONPs coated by either citrate anions (Cit sample—continuous line) or PEG (PEG sample—dashed line). TEM volume size distribution was fitted by log-normal law

References

- [1] H. Ezzaier, J. Alves Marins, S. Schaub, B. H. Amara, P. Kuzhir, *J. Mag. Mat.* 2018, 459, 350
- [2] G. Hemery, A. Keyes, E. Garaio, I. Rodrigo, J. A. Garcia, F. Plazaola, E. Garanger, O. Sandre, *Inorg. Chem.* 2017, 56, 8232
- [3] G. Hemery, C. Genevois, F. Couillaud, S. Lacomme, et al. *Mol. Sys. Des. Eng.* 2017, 2, 629-639
- [4] H. Ezzaier, J. Marins, C. Claudet, G. Hemery, O. Sandre, P. Kuzhir, *Nanomaterials* 2018, 8, 623

Grafting and Characterizations

"mushroom" $\Sigma = \frac{\pi R_g^2}{d^2}$

"brush" $\Sigma = \frac{\pi R_g^2}{d^2}$

Reduced tethered density (σ)

Porod regime in small-angle neutron scattering (SANS)

Magnetization curves of aqueous suspensions of multicore IONPs coated by ether citrate anions or PEG. Solid line: Fröhlich-Kennely fit Dashed line: Langevin fit

Parameters of DLVO and magnetic dipolar interactions

Coating	Separation between IONPs h = 2δ (nm)	Debye Length κ ⁻¹ (nm)	Charge Density q (mC/m ²)	Van der Waals Energy U _{vaw} / (k _B T)	Electrostatic Energy U _{el} / (k _B T)
Cit	0.4	2.3	9.5	11.6	25.4
	2.0			2.3	7.5
	6.8 (mushroom)			0.7	0.6
PEG	12.0 (DLS-TEM)	4.0	3.4	0.4	0.15
	15.6 (brush)			0.3	0.06

$H_0 = 4.2$ kA/m

Coating	Separation between IONPs, h [nm]	Moment $m_{NP} \times 10^{24}$ [T x m ³]	Langevin parameter ξ	Dipolar parameter λ_1	Dipolar parameter λ_0	Moment $m_{NP} \times 10^{24}$ [T x m ³]	Langevin parameter ξ	Dipolar parameter λ_1	Dipolar parameter λ_0		
Cit	0.4 (a)	1.22	0.62	1.15	1.10	2.04	3.33	3.22	3.08		
	2.0 (b)									0.93	2.60
	6.8 (c)									0.64	1.55
PEG	12.0 (d)	1.27	0.64	1.25	0.42	1.98	3.23	3.04	1.01		
	15.6 (e)									0.32	0.77

$H_0 = 13.5$ kA/m

Kinetics of Aggregation: Aggregate Size

Snapshots of aqueous suspensions of citrated (a) and PEGylated (b) IONPs at particle volume fraction $\phi_0 = 0.17 \pm 0.03$ vol.% subjected to an external uniform magnetic field of intensity $H_0 = 13.5$ kA/m. Each row corresponds to the elapsed time from the moment of the magnetic field application $t = 0$ (upper row), 5, 10, 15 and 20 min (bottom row).

Experimental and theoretical dependencies of the aggregate length on the elapsed time since the beginning of magnetic field application for the citrated and the PEGylated samples respectively, at the same nanoparticle volume fraction $\phi_0 = 0.17 \pm 0.03$ vol.% and at the intensity of the applied magnetic field $H_0 = 13.5$ kA/m.

Deposit growth around the micropillar and filter efficiency

Capture efficiency of bulk needle-like aggregates

-Mason number Ma : ratio of hydrodynamic to magnetic forces exerted on individual IONPs

-Capture efficacy: fraction of IONPs in flow that are deposited around the magnetic micropillar

$\Lambda_c \sim \left(\frac{\Delta_0}{\lambda_0} \right)^{3/2} \frac{L_c}{d_0} \frac{d_0}{d_1} P_e^{-4/3} Ma^{-1} \left(\frac{\Delta_0}{\lambda_0} \right)^{1/2} Ma^{-1/7}$

Conclusions

1. Thinner citrate layer on the IONP surface promotes faster & stronger field-induced aggregation, resulting in longer & thicker needle-like aggregates as compared to those obtained with a thicker PEG layer. This is explained by an increase of the aggregation rate thanks to increased initial supersaturation Δ_0 of the suspension as the magnetic interaction dipolar coupling parameter λ_0 becomes stronger for IONPs covered with a thinner molecular layer.
2. Magnetic separation of MNPs realized in a microfluidic channel equipped with a single magnetizable micropillar. Measurements of the size of the nanoparticle deposits around micropillars allowed determining the capture efficiency Λ and the retention capacity S_{ret} , both decreasing with increasing Mason number due to stronger hydrodynamic/weaker magnetic forces hindering attraction of IONPs to the micropillar. Both theory and experiments confirm initial hypothesis that capture efficiency is significantly improved if MNPs undergo field-induced aggregation, whose timescale (several minutes) was comparable to travel time through the microfluidic separator.
3. Retention capacity is higher for the IONPs covered by a thinner citrate layer than for IONPs covered by a thicker PEG. This phenomenon is attributed to the fact that at same Mason number, dipolar coupling parameter of the Cit sample is about 2–3 times higher than for the PEG sample ($\lambda_0 = 2.60$ – 3.08 vs. 0.77 – 1.55). Stronger dipolar magnetic interactions between citrated MNPs allow to better resist against rupturing hydrodynamic forces on deposit surface.
4. On the contrary, the capture efficiency appears to be almost the same for thick PEG and thin citrate layers on the IONPs surface over the wide range of Mason numbers studied ($300 < Ma < 10^4$). A small difference between both samples is explained by the fact that only a small portion of MNPs composes aggregates. Theoretical model developed in this work predicts a power-law trend of the Mason number dependency for the capture efficiency with exponent $11/7 \approx 1.57$ in agreement with the experimental dependency at $300 < Ma < 10^4$.
5. Finally, current work clearly shows that multicore IONPs of ~30 nm size synthesized by the polyol route show good potential for biomedical sensor uses where efficient magnetic separation at low-field is required. On needs to find a compromise between biological functionalities of the adsorbed molecular layer and magnetic separation efficiency.