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

O. Sandre,*1 Gauvin Hémery,1 Vincent Manin,1 Hinda Ezzaier,2 Cyrille Caludet,2 Pavel Kuzhir*2

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,10 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. 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 kBT. 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-filer across a microchannel submitted to a uniform external magnetic field H0. 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.14

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

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**ImmuoMag project (funded by UCA/CEDIR IdEx)**

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

**Capture of antigens by Agglutinated MNPs and detection by secondary Ab**

Principle stages of microfabrication of a microfluidic channel. (b) deposits of ONPs around the micropillar (deposit surface area is in hatched).

**Parameters of DLVO and magnetic dipolar interactions**

<table>
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<th>Coating</th>
<th>Separation (nm)</th>
<th>Charge parameter (nm)</th>
<th>Dipolar parameter (nm)</th>
<th>Charge parameter (nm)</th>
<th>Dipolar parameter (nm)</th>
</tr>
</thead>
<tbody>
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<td>0.6</td>
<td>1.2</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>PEG</td>
<td>0.6</td>
<td>0.6</td>
<td>1.2</td>
<td>0.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**Grafting and Characterizations**

**Conclusions**

1. Thinner layer on the IDNP 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 superheating of the suspension as the magnetic interaction dipolar coupling parameter λ decreases strongly for Cr for CrO3 for metal core layers.
2. Magnetic separation of MNPs realized in a microfluidic channel equipped with a single magneticable micropillar. Measurements of the size of the nanoparticle deposits around micropillars allowed determining the capture efficiency and the retention capacity, both drying with increasing Mason number due to stronger hydrodynamic weakening of magnetic forces limiting attraction of MNPs to the micropillar. Both theory and experiments confirmed this behavior for CrO3 and PEG coated iron oxide micropillars. In the case of CrO3, the retention capacity of the micropillar decreased with increasing thickness of the organic layer coating the micropillar. This phenomenon is attributed to the fact that a larger Mason number dipolar coupling parameter of the CrO3 is about 2.6 times stronger than that of PEG coated iron oxide micropillar.

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**Magnetic separation of multicore iron oxide nanoparticles (IDNP) at particle volume fraction 15.6% (brush) and 6.8% (mushroom)**

**Quantity of magnetic separation at equilibrium**

Volume size distribution of multicore iron oxide nanoparticles (IDNP) measured by TEM and SEM (left). The hydrodynamic size distribution was measured by DLS on IDNP coated by either CrO3 or PEG (right). TEM volume size distribution was fitted log-normal law

**Kinetics of Aggregation: Aggregate Size**

Snapshots of aqueous suspensions of citrated (a) and PEGated (b) IONPs at particle volume fraction 15.6% (brush) and 6.8% (mushroom). Each row corresponds to the elapsed time at moment of the magnetic field application t = 0 (top), 5, 10, 15 and 20 min (bottom row).

**Deposit growth around the micropillar and filter efficiency**

Graphs of the deposits of strontium(stand) or Plutonium(2) IDNP around a single magneticized micropillar in the microfluidic channel under hydrodynamic flow and intermicellar magnetic field of intensity of 13.5 kA/m. Both size and coverage are found to be significantly lower by a factor of 3.7 to 0.65 for Sr. The rows of (a) and (c) correspond to different elapsed times from the top to the bottom (t = 0, 5, 10, 20, and 60 min), the columns correspond different flow speeds (v0 = 0.17, 0.34, 0.68, 1.33, 2.63, and 10 m/s).