Electronic Supplementary Material (ESI) for Lab on a Chip.

Electronic supplementary information for

Magnetic microreactors for efficient and reliable magnetic nanoparticles surface functionalization

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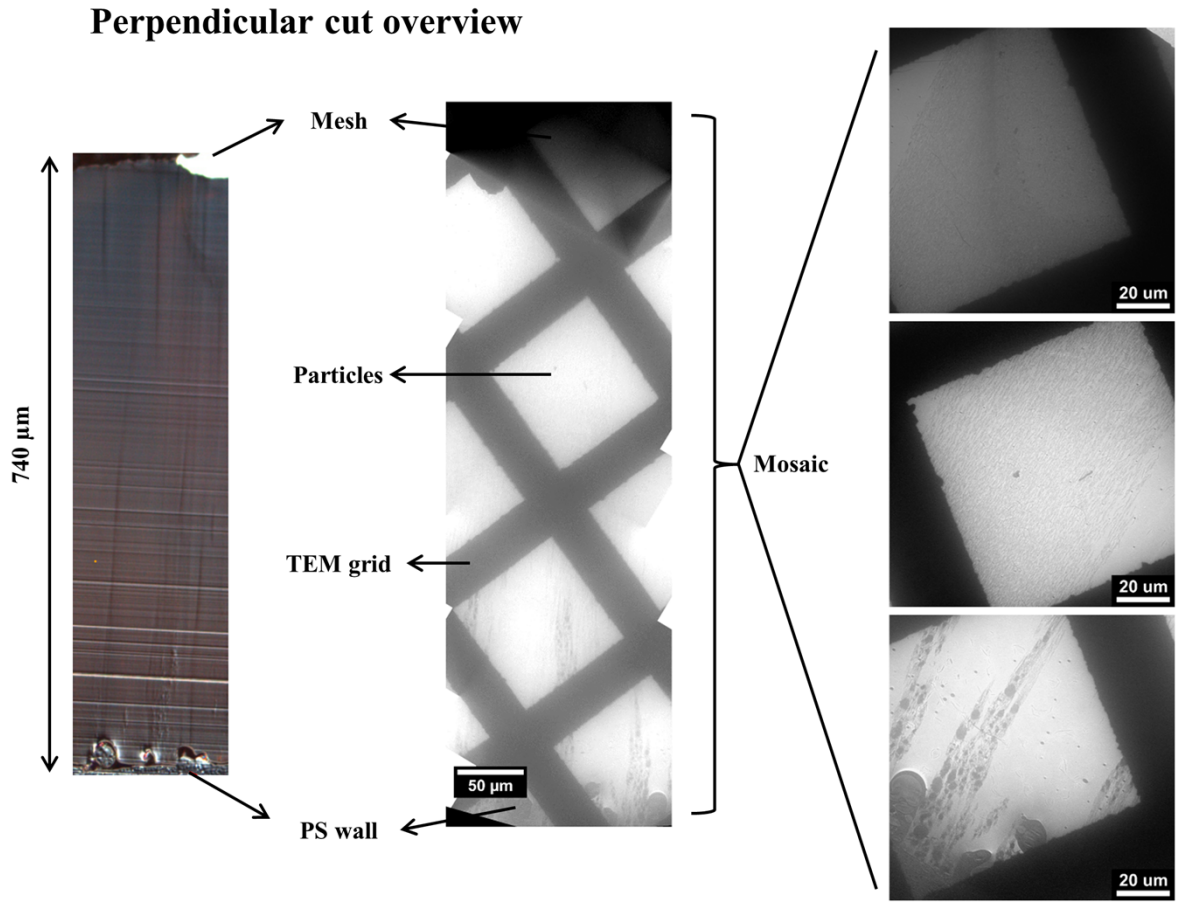

Figure SI-1: Magnetic alignment of the NPs – TEM slice cut overview.

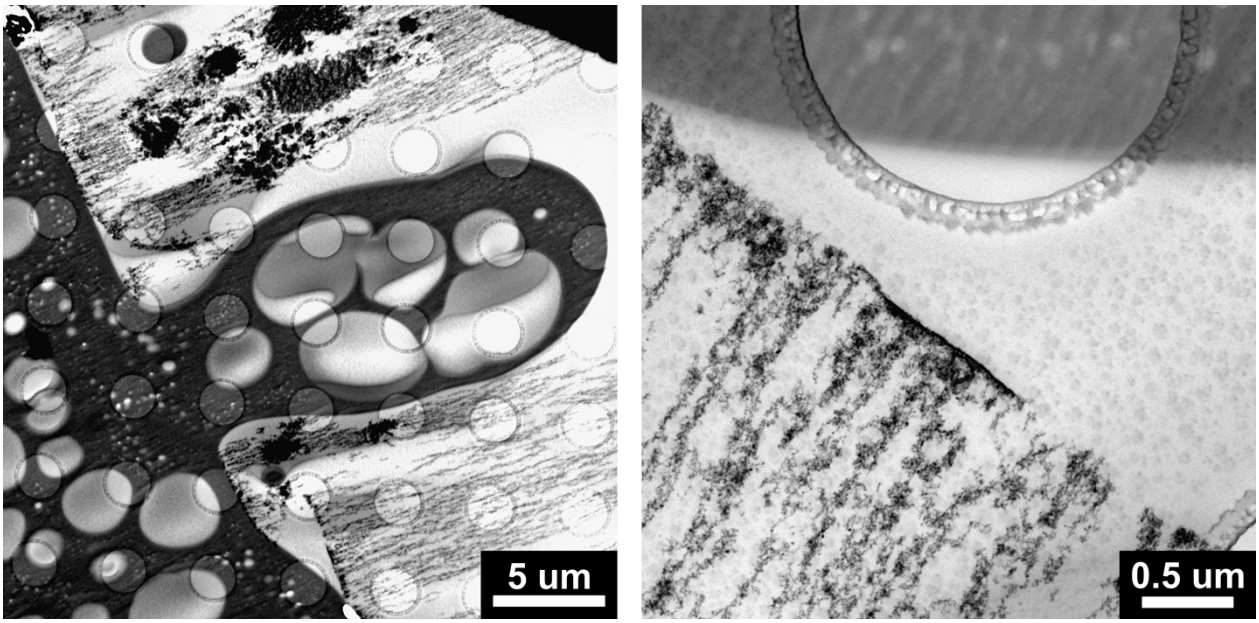

Figure SI-2: TEM images of the alignment of the NPs inside the micro reactor (abrupt stop at the PS wall).

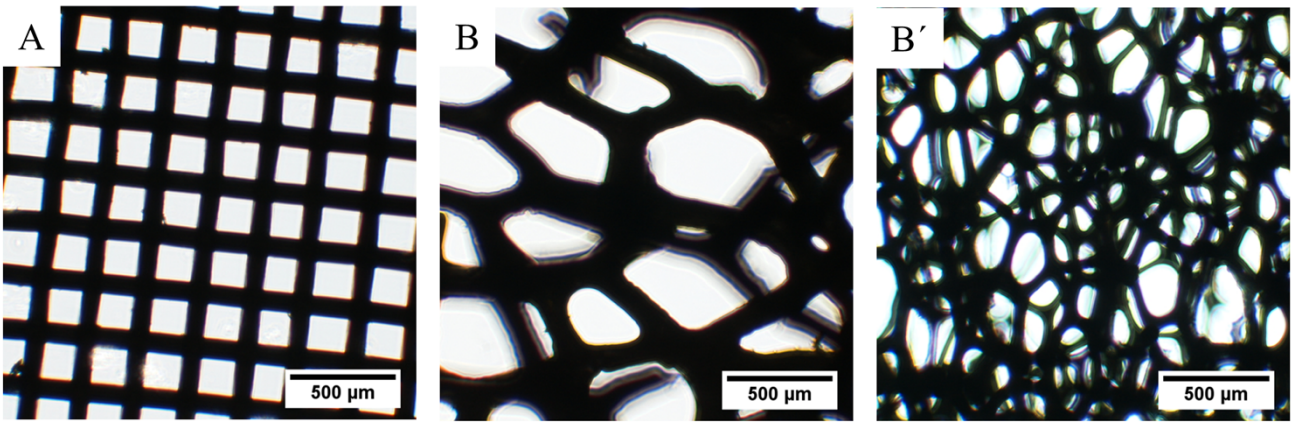

Figure SI-3: Light microscopy images of the Ni Mesh (A) and Ni foam (B and B´).

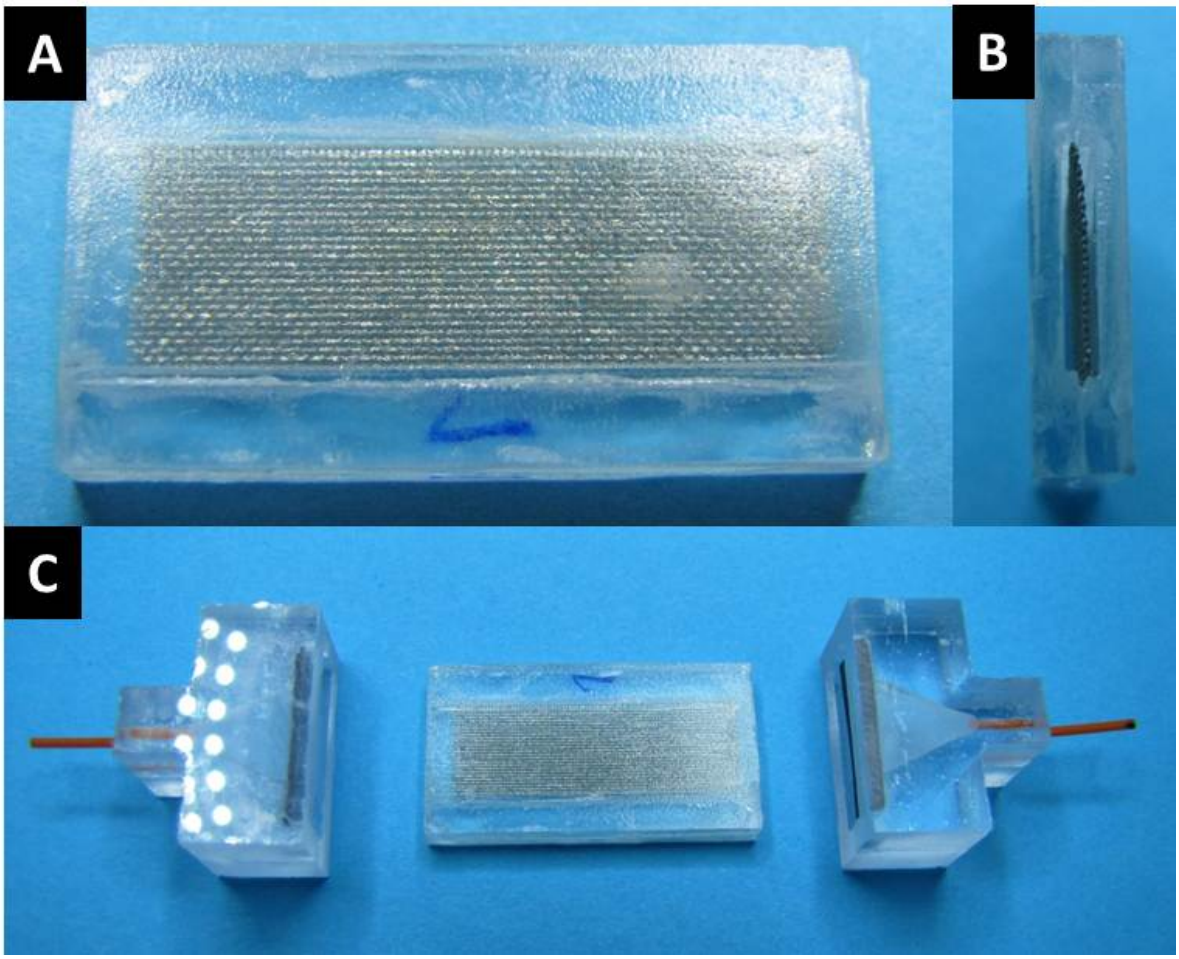

Figure SI-4: Digital pictures of different elements of the microreactor chamber. A and B: Top and side views of the chamber with Ni mesh inside. C: Microreactor chamber with connectors.

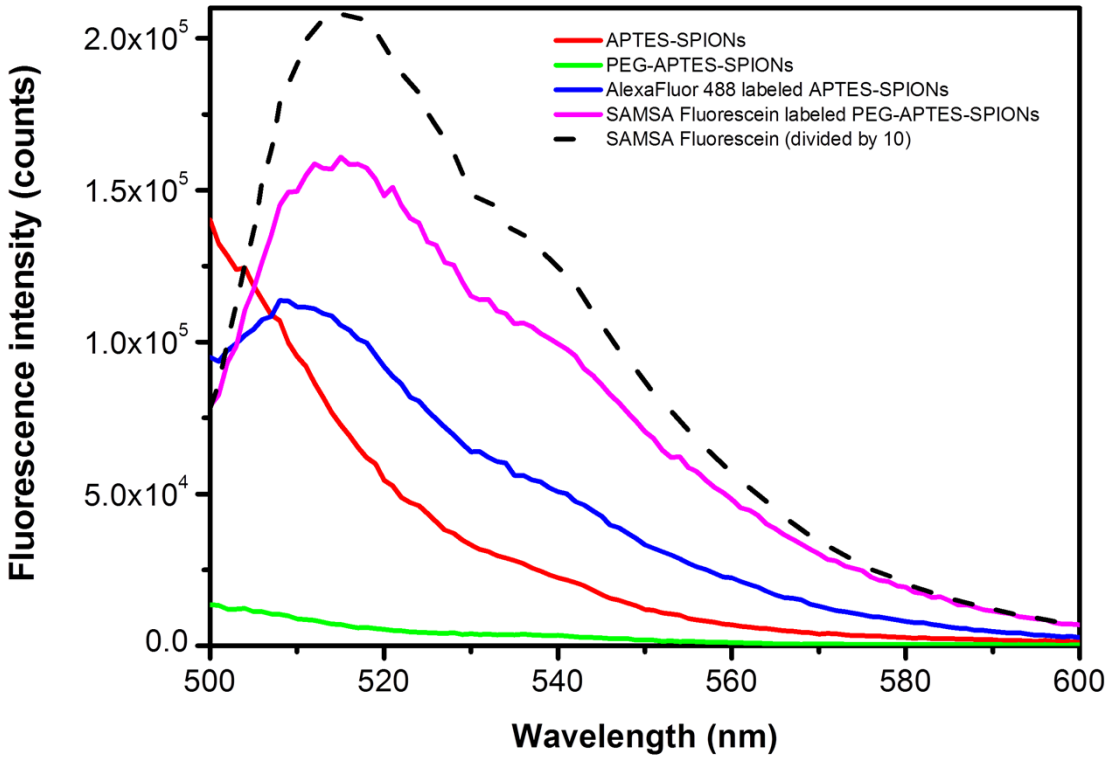

Figure SI-5: Fluorescence spectra of APTES-SPIONs (red), PEG-APTES-SPIONs (green), AlexaFluor 488 labeled APTES-SPIONs (blue), SAMSA fluorescein labeled PEG-APTES-SPIONs (purple) and SAMSA fluorescein (black dotted line, values divided by 10) measured at λ_{exc}=490 nm.

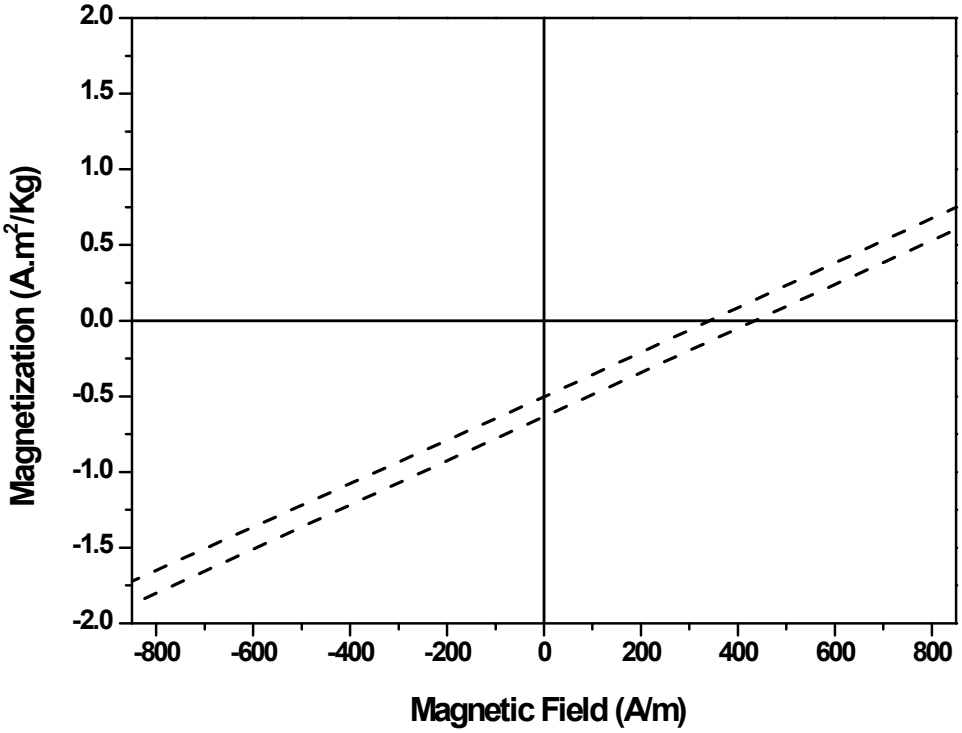

Figure SI-6: Magnification of the magnetization curve of the APTES-coated SPIONs.

Reactor type	Version A - Mesh															
Flow rate (mL/min)	0.1				0.5				0.5				1			
Total Volume loaded (mL)	5				5				10.0				5			
Circulation time (hour)	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24
Iron Trapped (ug)	1324	1903	2394	2417	873	1559	1787	2097	669	1810	2346	2808	717	1337	1841	2439
Trap. efficiency (%)	***52.1***	***75.7***	***95.6***	***96.5***	***33.9***	***61.7***	***71.0***	***83.5***	***12***	***32.4***	***42.0***	***50.3***	***27.5***	***52.7***	***73.2***	***97.4***
Reactor type	Version B - Foam 50 PPI															
Flow rate (mL/min)	0.1				0.5				0.5				1			
Total Volume loaded (mL)	5				5				10.0				5			
Circulation time (hour)	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24
Iron Trapped (ug)	896	1732	2068	2071	868	1513	1727	1805	1081	1086	1567	2221	368	580	569	1050
Trap. efficiency (%)	***34.8***	***68.7***	***82.4***	***82.2***	***33.6***	***60.1***	***69.0***	***70.9***	***19.4***	***19.5***	***28.1***	***39.8***	***13.3***	***22.0***	***21.4***	***41.1***
Reactor type	Version B´ - Foam 100 PPI															
Flow rate (mL/min)	0.1				0.5				0.5				1			
Total Volume loaded (mL)	5				5				10.0				5			
Circulation time (hour)	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24	0.5	2	6	24
Iron Trapped (ug)	1097	1921	2366	2429	912	1558	2033	2232	445	887	2320	2552	494	555	843	2088
Trap. efficiency (%)	***42.9***	***76.4***	***94.4***	***97.0***	***35.4***	***61.6***	***80.9***	***89.5***	***8.5***	***16.9***	***44.3***	***48.7***	***18.5***	***20.9***	***32.6***	***83.0***

Table SI-1 – Trapping efficiency for each version of microreactor, calculated at different flow rate and circulation time.

Numerical simulations

In order to describe in a rigorous manner the time dependence of the nanoparticles concentration *n* profile around a magnetized wire, a two-dimensional partial differential equation needs to be solved. Its solution allows one to monitor the kinetics of buildup accumulation directly, by integrating over the entire region in space where the nanoparticles concentration is above the bulk value. The equation to be solved is the following:

$$\frac{\partial n}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(r\left(D(\phi)\frac{d\Pi}{d\phi}\frac{\partial n}{\partial r}-v_r(r,\varphi)n+\frac{D(\phi)}{kT}\frac{\partial U_M}{\partial r}n\right)\right)+ \quad \backslash*$$
$$\frac{1}{r}\frac{\partial}{\partial \varphi}\left(D(\phi)\frac{1}{r}\frac{d\Pi}{d\phi}\frac{\partial n}{\partial \varphi}-v_\varphi(r,\varphi)n+\frac{D(\phi)}{kT}\frac{1}{r}\frac{\partial U_M}{\partial \varphi}n\right)$$

MERGEFORMAT (1.1)

where *r* is the distance from the wire center, and ϕ is the polar angle. The magnetic interaction energy of a nanoparticle with a magnetized wire subject to an external magnetic field H_0 is given by:

$$U_M(r,\theta)=-\frac{2\pi\mu_0 M_p M_w R_p^3 R_w^2}{3r^2}\left(\frac{M_w R_w^2}{4H_0 r^2}+\cos(2\theta)\right) \quad \backslash*$$

MERGEFORMAT (1.2)

while the velocity profile is given by:

$$v_r(r,\varphi)=-V_0\frac{\log\frac{r}{R_w}-\frac{1}{2}\left(1-\left(\frac{R_w}{r}\right)^2\right)}{2-\log(\mathrm{Re})}\sin(\varphi) \quad \backslash*$$
$$v_\varphi(r,\varphi)=-V_0\frac{\log\frac{r}{R_w}+\frac{1}{2}\left(1-\left(\frac{R_w}{r}\right)^2\right)}{2-\log(\mathrm{Re})}\cos(\varphi)$$

MERGEFORMAT (1.3)

In Equation (3), V_0 is the velocity of fluid at infinite distance from the wire. In both equations (1) and (2) and (3) the symbols are the same as in the main text. Equation (1) is subject to the initial condition stating that the particles concentration is initially equal to n_0 everywhere, as well as to the following boundary conditions:

$$\begin{cases}\left.\frac{d\Pi}{d\phi}\frac{\partial n}{\partial r}+n\cdot\frac{\partial U_M}{kT\partial r}\right|_{r=R_w}=0 \\ n(r=d)=n_0\end{cases} \quad \backslash*$$

MERGEFORMAT (1.4)

The first of Equations * MERGEFORMAT (1.4) states that the overall flux at the wire surface has to be equal to zero; while the second one imposes that the concentration of particles at a distance d sufficiently far away from the wire surface equals the bulk concentration.

Before a numerical solution, equation (1) needs to put in dimensionless form. We define: $u=n/n_0$, $\xi=r/R_w$, $Pe=R_w \cdot V_0/D_0$ and $\tau=t \cdot D_0/R_w^2$. This leads to:

$$\frac{\partial u}{\partial \tau}=\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\left(f(\phi)\frac{d\Pi}{d\phi}\frac{\partial u}{\partial \xi}-v_r(\xi,\varphi)u+\frac{D(\phi)}{kT}\frac{\partial U_M}{\partial \xi}u\right)\right)+$$
$$\frac{1}{\xi}\frac{\partial}{\partial \varphi}\left(f(\phi)\frac{1}{\xi}\frac{d\Pi}{d\phi}\frac{\partial u}{\partial \varphi}-v_\varphi(\xi,\varphi)u+\frac{D(\phi)}{kT}\frac{1}{\xi}\frac{\partial U_M}{\partial \varphi}u\right) \quad \text{*}$$

MERGEFORMAT (1.5)

Equation * MERGEFORMAT (1.5) has been solved using a forth order finite difference scheme, as follows:

$$\left.\frac{\partial u}{\partial \xi}\right|_{\xi=\xi_i}=\frac{u_{i-2}-8u_{i-1}+8u_{i+1}-u_{i+2}}{12\Delta\xi}$$
$$\left.\frac{\partial^2 u}{\partial \xi^2}\right|_{\xi=\xi_i}=\frac{-u_{i-2}+16u_{i-1}-30u_i+16u_{i+1}-u_{i+2}}{12\Delta\xi} \quad \text{*}$$
$$\left.\frac{\partial u}{\partial \varphi}\right|_{\varphi=\varphi_j}=\frac{u_{j-2}-8u_{j-1}+8u_{j+1}-u_{j+2}}{12\Delta\varphi}$$
$$\left.\frac{\partial^2 u}{\partial \varphi^2}\right|_{\varphi=\varphi_j}=\frac{-u_{j-2}+16u_{j-1}-30u_j+16u_{j+1}-u_{j+2}}{12\Delta\varphi}$$

MERGEFORMAT (1.6)

Initially, the dependence of the diffusion coefficient (Equation (6) in the main text) and the correction of the osmotic pressure due to high particle concentration have been neglected. This leads to a linear equation, which can be discretized into a large system of ODEs, as follows:

$$\frac{\partial \mathbf{u}}{\partial \tau}=\mathbf{M}\cdot\mathbf{u}+\mathbf{b} \quad \text{*}$$

MERGEFORMAT (1.7)

An implicit Euler method has been used to solve this system of equations.

$$\mathbf{u}_n=\left(\mathbf{I}-\Delta\tau\mathbf{M}\right)^{-1}\left(\mathbf{u}_{n-1}+\Delta\tau\mathbf{b}\right) \quad \text{*}$$

MERGEFORMAT (1.8)

The equations have been solved using a home-made finite difference code programmed in FORTRAN (Intel FORTRAN Parallel Studio 2011). A very fine spatial grid has been utilized,

with up to 400000 grid points. In order to deal with the large memory occupancy resulting from the discretization, a sparse matrix approach has been used to store the coefficients of the discretized equation.

The solution of equation * MERGEFORMAT (1.5) is highly time-consuming. Therefore it has only been performed for a few representative operative conditions with the objective to obtain a steady state concentration profile, from which an angular average effective radial velocity profile can be obtained. The angular average velocity has been obtained from the following equation:

$$\overline{v}_r(r) = \frac{\int_0^{2\pi} v_r(r,\varphi)\cdot n(r,\varphi)d\varphi}{\int_0^{2\pi} n(r,\varphi)d\varphi} \qquad \text{* MERGEFORMAT (1.9)}$$

The values have then been then fitted by means of the semi-empirical expression (7) reported in the main text.

Having an angular average velocity, together with the angular average magnetic energy, defined by Equation (6) in the main text, allows one to solve the one dimensional and steady state version of the diffusion-convection equation, Equation (4) in the main text. Its solution provides an angular average concentration profile, which allows the estimation of the amount of particles accumulated around a wire under a given condition. A critical distance r^* is estimated, as the value such that the amount of particles accumulated around a wire is equal to a given amount.

The rate of trapping K, appearing in Equations (1) e (2), is estimated as follows:

$$K = \frac{D(\phi)}{kT}\frac{dU_M}{dr}n - \overline{v}_r(r)n\Big|_{r=r^*} \qquad \text{* MERGEFORMAT (1.10)}$$

This implies that is assumed that the build-up, i.e., the amount of particles accumulated around the wires, is increasing in a layer-by-layer fashion. Therefore, when the amount of particles reaches the maximum possible under certain conditions, the rate of trapping K equals zero.