ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Cooperative Switching in Large-Area Assemblies of Magnetic Janus Particles

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Electrohydrodynamic co-jetting

Magnetic Janus particles and microcylinders were prepared by modifying previously established methods.[23,28,39] In brief, all jetting materials were dissolved in a solution of given solvents with concentrations as shown in **Table 1-2**. Two jetting suspensions were separately pumped through a dual capillary system [26 gauge needle (Hamilton Comp.) for particle jetting, or 23 gauge needle (Nordson EFD Corp.) for fiber jetting] held together in a side-by-side geometry. The capillaries were connected to the cathode of a DC voltage source (Gamma High Voltage Research, USA) and the flow rate was controlled via a syringe pump (Kd Scientific, USA). A flat piece of aluminum foil was used as a counter electrode. The distance between the capillary tip and the substrate was maintained in the range of 40 cm for producing the particle, and 10 - 15 cm for fabricate the microfiber. All experiments were performed at room temperature (23 – 25 °C). The polymer solutions were delivered at a given flow rate with a driving voltage (see **Table 1 - 2**). The resulting particles (or fibers) were collected and dried under vacuum for overnight. To make microcylinders, the microfibers solidified in a medium (Tissue-Tek O.C.T. Compound, Andwin Scientific, USA) were mounted onto a cryostat chuck at -20 °C, and sectioned by a cryostat microtome (HM550 OMC, Microme) with a given length (450 µm). The processed particles were suspended in an aqueous solution containing Tween 20 (2 v/v %) prior to use.

Table 1 Experimental conditions for electrohydrodynamic co-jetting to prepare MJPs with 20 µm in diameters.

	Green	Red
PLGA, wt/v %in chloroform : methylene chloride(= 50 : 50, v/v)	9	9
Functional components, wt/v %	PTDPV, 0.01	ADS306PT, 0.01 F_3O_4, 0.45
Applied Voltage, kV	6	
Flow Rate, ml/h	3	

Table 2 Experimental conditions for electrohydrodynamic co-jetting to prepare bi-compartmentalized magnetic microfibers having yellow/black colorants with 450 µm in diameters.

	Yellow	Black
PLGA, wt/v % in chloroform: DMF (= 95 : 5, v/v)	35	35
Functional components, wt/v %	Yellow 14, 10	CB, 2.6 F_3O_4, 1.0
Applied Voltage, kV	9 ~ 10	
Flow Rate, ml/h	0.05	

Characterization

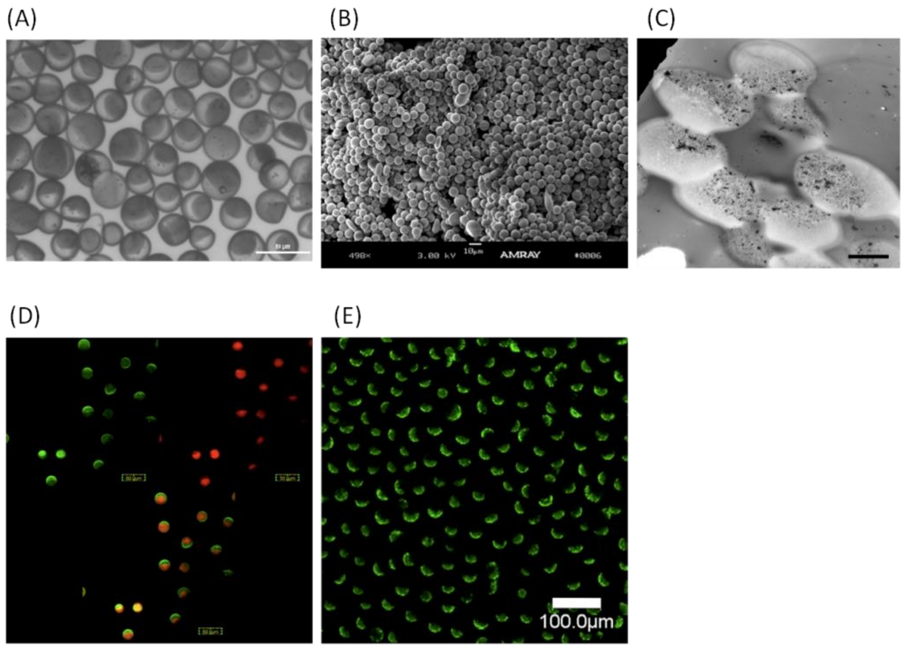

Fig. S1 Various micrographs of magnetic Janus particles. (A) Optical microscopy (OM, nikon TE2000) elucidates anisotropic compartmentalization of magnetite nanocrystals in the PLGA particles. Magnetite nanocrystals are located in the darker side. (B) Scanning electron microscopy (SEM; Nova Nanolab DulBeam, 3 kV) confirms the round shapes of the MJPs. (C) Transmission electron microscopy (TEM, Philips CM-100, 60 kV); The particles were randomly mixed in epoxy resin. The microtomed image exhibits that the particles are randomly positioned, and magnetite nanoparticles are dispersed in one compartment of the particles. Scale bar represents 10 μm. (D – E) Confocal laser scanning microscopy (CLSM, Olympus Fluoview 500) was used to analyze the particles in DI water. The fluorescence dyes, PTDPV for green and ADS306PT for red were excited by 488 nm Argon and 533 nm Helium-Neon, respectively. Optical filters of emission wavelength, 505–525 and 560–600 nm, were used to visualize the fluorescence of PTDPV and ADS306PT, respectively. (D) The top left window shows green fluorescent areas of the particles (non-magnetic compartment). The top right window demonstrates red fluorescent parts of the particles (magnetic compartment). The bottom window is superimposed image of both green and red windows, showing that the particles are highly compartmentalized. (E) CLSM image of the green channel corresponding to Fig. 1.

Simulated assemblies of MJPs

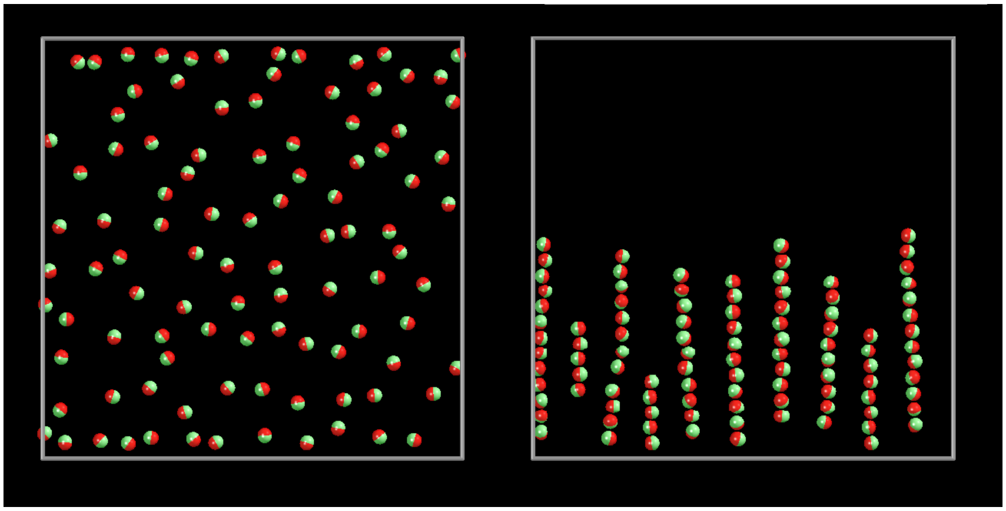

Fig. S2 Simulated assemblies based on the newly developed simulation model reproduce the well-known experimental results. Assembled structures formed when **B** is uniform and perpendicular to the viewing plane, the z-axis (left) and when B is parallel to the y-axis and the particle dipoles are strong (right).

1. Details related to Computer Simulations

In the following, we analyze the order of magnitude of the forces between the magnetic Janus particles at the micrometer scale. The interactions basically include the dipole-dipole repulsion, particle-magnetic field, frictions and excluded volume interaction, i.e. the force preventing the particles from overlapping. From the order of magnitude analysis, we introduce the dimensionless quantities used in our Molecular Dynamics (MD) simulation, followed by the discussion on choosing a reasonable force and time scale so that simulation can tackle those in experiment in a practical amount of CPU time.

1.1. Dipole-dipole interaction

Consider two magnetic particles placed on the x axis separated by a distance of their diameter $d = \sigma$. When their dipoles are parallel to each other, the interacting force between two particles is:

$$F_d = \frac{3\mu_0}{4\pi d^4}\mu_i\mu_j$$

From the magnetization hysteresis, the particle magnetization is approximately m_v = 10×10^{-3} emu/cm^3, with the particle size being 20×10^{-6} m, the particle dipole moment is μ_i = 10×10^{-3} emu/cm^3 × π/6 × $(20\times10^{-6})^3$ m^3 = 10 A/m × 4×10^{-15} m^3 = 4×10^{-14} Am^2. F_d can then be estimated by:

$$F_d = \frac{3\times 4\pi\times 10^{-7}}{4\pi\times 16\times 10^{-20}\ m^4}\times 16\times 10^{-28}A^2m^4 = 3\times 10^{-15}\ N = 0.003\ pN$$

That means two magnetized particles touching each other repel with a force equal to F_d = 0.003 pN.

1.2. Magnetic field

The gradient magnetic field **B**(x) = (B + a · x)$\mathbf{e}_z$ exerts on each particle an additional force:

$$F_b = \frac{\partial(\mu_i(B + a\cdot x))}{\partial x} = \mu_i\cdot a$$

For $\mu_i = 4\times10^{-14}$ Am^2 and a = 1 T/m = 1 Am^2, F_b can be estimated by:

$$F_b = 4\times 10^{-14}\ Am^2\times 1\ A/m^2 = 4\times 10^{-14}N = 0.04\ pN$$

Considering the interaction range of the dipole-dipole interaction in the order of 10σ, resulting in the net repulsion force exerting on a particle being in the order of (10 − 100) F_d, this value of F_b is possible to induce a close packing.

1.3. Friction

As the particles move under the gradient field, they are subject to friction and thermal motion due to solution molecules. While the thermal random forces are small as compared to the particle length scale, the friction might be significant.

$$F_v = -\gamma v_i = -3\pi\zeta\sigma \cdot v_i$$

For $\zeta_{water} = 10^{-3}$ Ns/m^2 at 25°C and $v_i = 10\times10^{-6}$ m/s:

$$\begin{aligned} F_v &= -3\pi \times 10^{-3}\ Ns/m^2 \times 2 \times 10^{-5}\ m \times 10 \times 10^{-6}\ m/s \\ F_v &= 1\ pN \end{aligned}$$

Note that although F_v seems to be much greater than F_d and F_b, it is active only when the particles move, and hence serves as a damper for the system.

1.4. Excluded volume interaction

The excluded volume interaction is modeled by the Weeks-Chandler-Anderson potential:

$$F_{ex} = \frac{4\epsilon}{d}\left[12\left(\frac{\sigma}{d}\right)^{12} - 6\left(\frac{\sigma}{d}\right)^{6}\right]$$

For two particles touching each other $d = \sigma$.

$$F_{ex} = \frac{24\epsilon}{\sigma}$$

The magnetic field F_b should not be greater than the excluded volume force to avoid nonphysical overlapping, meaning that

$$F_{ex} = \frac{24\epsilon}{\sigma} = F_b = 0.04\ pN$$

yielding

$$\epsilon = \frac{F_b\sigma}{24} = 0.04 \times 10^{-12}\ N \times 2 \times 10^{-5}\ m/24 = 3.3 \times 10^{-20} J$$

2. Simulation parameters

2.1. Dipole-dipole interaction

Define the dimensionless dipole moment as

$$m_i = \frac{\mu_i}{k\sqrt{\sigma^3\mu_i B}}$$

with k being some scaling factor, plugging into equation 1

$$F_d = \frac{3\mu_0}{4\pi r^4\sigma^4} m_i m_j k^2\sigma^3\mu_i B = \left(\frac{3}{r^4} m_i m_j\right)\frac{k^2\mu_0\mu_i B}{4\pi\sigma}$$

2.2. Magnetic field

$$\begin{aligned} F_b &= \mu_i \cdot a = m_i k\sqrt{\sigma^3\mu_i B}\cdot a = m_i \cdot a\sqrt{\sigma^3\mu_i B}\frac{4\pi\sigma}{k\mu_0\mu_i B}\frac{k^2\mu_0\mu_i B}{4\pi\sigma} \\ F_b &= m_i \cdot a \cdot \frac{4\pi}{\mu_0 k}\sqrt{\frac{\sigma^5}{\mu_i B}}\cdot\frac{k^2\mu_0\mu_i B}{4\pi\sigma} = (m_i g_B)\cdot\frac{k^2\mu_0\mu_i B}{4\pi\sigma} \end{aligned}$$

where g_B, the dimensionless field gradient, is defined as:

$$g_B = a\cdot\frac{4\pi}{\mu_0 k}\sqrt{\frac{\sigma^5}{\mu_i B}}.$$

For $\mu_i = 4\times10^{-14}$ Am^2 and $k = 1$:

$$\begin{aligned} m_i &= \frac{4\times10^{-14}\ Am^2}{1\times\sqrt{8\times10^{-15}\ m^3\ 4\times10^{-14}\ Am^2\ 0.1\ A/m}} \\ m_i &= 4\times10^{-14}\ Am^2\times3.53\times10^{14}/Am^2 \\ m_i &= 15 \end{aligned}$$

A value of a = 20 mT/5 cm = 1 T/m in experiments and k = 1 correspond to:

$$\begin{aligned} g_B &= 1\ T/m\cdot\frac{1}{10^7\times1}\sqrt{\frac{32\times10^{-25}\ m^5}{4\times10^{-14}\ Am^2\ 0.1\ A/m}} \\ g_B &= 282 \end{aligned}$$

This value of g_B indeed gives a close packing for m_i = 15. Note that the forces are in the unit of

$$\frac{k^2\mu_0\mu_i B}{4\pi\sigma} = \frac{1^2\times10^{-7}\times4\times10^{-14}\ Am^2\times0.1\ A/m}{2\times10^{-5}\ m}$$

2.3. Friction

Define Δt as the time step, $\Delta t = 0.001\tau$ in the simulation with τ being the time unit, which is the time it take the particle to travel a distance equal to its diameter. The dimensionless velocity can be defined as $V_i = v_i\tau/\sigma$.

$$\begin{aligned} F_v &= -\gamma v_i = -3\pi\zeta\sigma\cdot V_i\frac{\sigma}{\tau}\cdot\frac{4\pi\sigma}{k^2\mu_0\mu_i B}\frac{k^2\mu_0\mu_i B}{4\pi\sigma} \\ F_v &= -\frac{12\pi^2\zeta\sigma^3}{k^2\mu_0\mu_i B\tau}V_i\frac{k^2\mu_0\mu_i B}{4\pi\sigma} = (-\gamma_{sim}V_i)\frac{k^2\mu_0\mu_i B}{4\pi\sigma} \end{aligned}$$

where

$$\gamma^{sim} = \frac{12\pi^2\zeta\sigma^3}{k^2\mu_0\mu_i B\tau}$$

is the dimensionless viscosity parameter used in our simulation.

2.4. Excluded volume interaction

The excluded volume interaction modeled by the Weeks-Chandler-Anderson potential is expressed in the chosen force unit:

$$F_{ex} = \frac{4\epsilon}{d}\left[12\left(\frac{\sigma}{d}\right)^{12} - 6\left(\frac{\sigma}{d}\right)^{6}\right]\frac{4\pi\sigma}{k^2\mu_0\mu_i B}\frac{k^2\mu_0\mu_i B}{4\pi\sigma}$$

$$F_{ex} = \frac{4\epsilon_{sim}}{r}\left[12\left(\frac{\sigma}{d}\right)^{12} - 6\left(\frac{\sigma}{d}\right)^{6}\right]\frac{k^2\mu_0\mu_i B}{4\pi\sigma}$$

where

$$\epsilon_{sim} = \frac{4\pi\epsilon}{k^2\mu_0\mu_i B} = \frac{3.3 \times 10^{-20} J}{1^2 \times 10^{-7} \times 4 \times 10^{-14}\ Am^2\ 0.1\ A/m} = 100$$

We can rescale m, g_B and $\varepsilon_{\mathrm{sim}}$ for smaller force values in simulations by using the scaling factor k greater than 1. For example, if $k = 10$ then the above values of m and g_B become m = 1.5, $g_B = 28.2$ and $\varepsilon_{\mathrm{sim}} = 1$.

2.5. Time scale

If we choose F_b as the characteristic force, the time unit can be estimated by the equation of motion:

$$M\frac{\sigma}{\tau^2} = \mu_i \cdot a$$

$$\tau = \sqrt{\frac{M\sigma}{\mu_i a}}$$

where M is the particle mass: $M = \rho\pi\sigma^3/6 = 1100\ \mathrm{kg/m^3} \times (20\times10^{-6})^3\ \mathrm{m^3} \times \pi/6 = 46\times10^{-12}$ kg, giving:

$$\tau = \sqrt{\frac{4.6 \times 10^{-12}\ kg \times 2 \times 10^{-5}\ m}{4 \times 10^{-14}\ Am^2 \times 1\ A/m^2}}$$

$$\tau = 0.05\ s$$

This value of τ and an estimate of $v_i = 10\times10^{-6}$ m/s give:

$$V_i = \frac{10 \times 10^{-6}\ m/s \times 0.05\ s}{2 \times 10^{-5}\ m}$$

$$V_i = 0.025$$

For $\zeta_{\mathrm{water}} = 10^{-3}\ \mathrm{Ns/m^2}$ at 25°C:

$$\gamma_{sim} = \frac{12\pi \times 10^{-3}\ Ns/m^2 \times 8 \times 10^{-15}\ m^3}{4 \times 10^{-7} \times 4 \times 10^{-14}\ Am^2\ 0.1\ A/m \times 0.05\ s}$$
$$\gamma_{sim} = 3.7 \times 10^6$$

The value of γ_{sim} is big because we choose F_b as the characteristic force, which is high as compared to the interacting force between the particles. Now if we choose the characteristic force as

$$\frac{k^2 \mu_0 \mu_i B}{4\pi\sigma} = 2 \times 10^{-17}\ N$$

then the time unit would be:

$$M\frac{\sigma}{\tau^2} = \frac{k^2 \mu_0 \mu_i B}{4\pi\sigma}$$
$$\tau = \sigma\sqrt{\frac{4\pi M}{k^2 \mu_0 \mu_i B}}$$

and for $k = 1$:

$$\tau = 2 \times 10^{-5}\ m \times \sqrt{\frac{4\pi \times 4.6 \times 10^{-12}\ kg}{1^2 \times 4\pi \times 10^{-7} \times 4 \times 10^{-14}\ Am^2 \times 0.1\ A/m}} \quad ($$
$$\tau = 2\ s \quad ($$

As a result, the velocity is rescaled as:

$$V_i = \frac{10 \times 10^{-6}\ m/s \times 2\ s}{2 \times 10^{-5}\ m} = 1$$

and the dimensionless viscosity

$$\gamma_{sim} = \frac{12\pi \times 10^{-3}\ Ns/m^2 \times 8 \times 10^{-15}\ m^3}{1^2 \times 4 \times 10^{-7} \times 4 \times 10^{-14}\ Am^2\ 0.1\ A/m \times 2\ s}$$
$$\gamma_{sim} = 9.25 \times 10^4$$

This value of γ_{sim} would cause a huge force exerting on the particles. By choosing a larger value of k, for instance, $k = 10$, we can rescale γ_{sim} accordingly as

$$\gamma_{sim} = 9.25 \times 10^2 = 925$$

which is reasonable for the time step of $\Delta t = 0.001\tau = 0.002$s.

3. Summary

For MD simulations, we choose $k = 10$, $m = 1–10$, $g_B = 10–100$, $\varepsilon_{\mathrm{sim}} = 10$ and $\gamma_{\mathrm{sim}} = 500$. $\varepsilon_{\mathrm{im}} = 10$ is chosen to make the particles effectively "harder" as they closely pack. The values are chosen so as to allow for the experimental parameters to be fully covered, as well as for the MD simulations to sample the experimental time scale within a practical amount of CPU time.