# Fabrication of Strong Magnetic Micron-sized Supraparticles with Anisotropic Magnetic Properties for Magnetorheology

J. R. Morillas,[1] E. Carreón-González[1,2] and J. de Vicente[1*]

[1]Biocolloid and Fluid Physics Group and Excellence Research Unit 'Modeling Nature' (MNat), Department of Applied Physics, Faculty of Sciences, University of Granada, C/Fuentenueva s/n, 18071 - Granada, Spain

[2]LANIMFE, Instituto de Física, Avenida Doctor Manuel Nava 6, Zona Universitaria CP 78290, San Luis Potosí, S.L.P, Mexico

jvicente@ugr.es

**Supplementary Material**

## Expected magnetic response of synthesized supraparticles

The magnetic response of the supraparticles based on non-magnetic ETPTA and magnetic carbonyl iron (CI) particles can be deduced from the magnetization curve of the latter as previously demonstrated in the literature [Tavacoli *et al*. (2013). *Soft Matter*, 9, 9103-9110]. For a CI volume fraction of $\phi$, supraparticle saturation magnetization $M_{sat}^{sup}$ and initial susceptibility $\chi_i^{sup}$ are given within a 4% of accuracy by:

$$M_{sat}^{sup} = \phi M_{sat}$$

$$\chi_i^{sup} = \phi \chi_i$$

being $M_{sat}$ and $\chi_i$ the CI particle saturation magnetization and the initial susceptibility, respectively. In Figure S1 it is shown the experimental magnetization cycle of the CI particles used in this work.

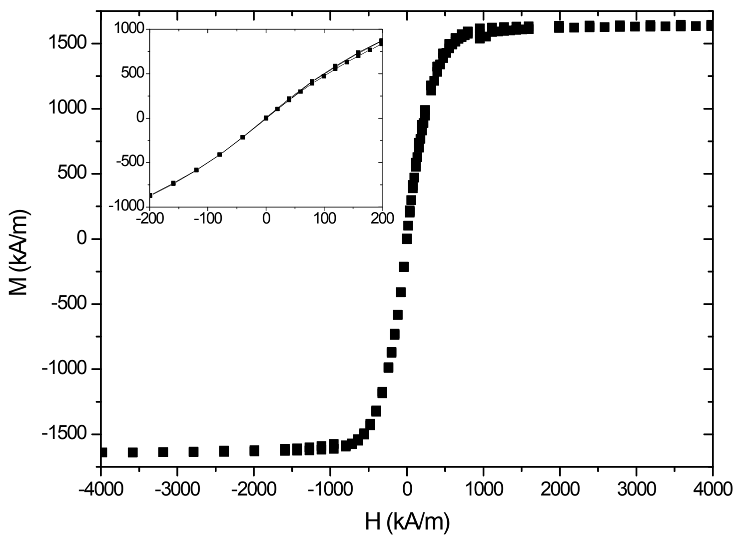


Figure S1: Magnetization curve for the powder CI particles (EW grade) used in this work.

From this figure it can be seen that $M_{sat} =$ 1600 kA/m and $\chi_i =$ 5.53 (up to 30 kA/m). This results in $M_{sat}^{sup} =$ 800 kA/m and $\chi_i^{sup} =$ 2.77 for the highest CI loading used in this work (50 vol%). These values are 20 and 4 times, respectively, the values already obtained in the literature for similar supraparticles obtained with microtransfer molding [Tavacoli *et al*. (2013). *Soft Matter*, 9, 9103-9110]. As expected, due to the microparticle size (around 5 μm) and nature (CI), microparticles and supraparticles do not show hysteresis at low fields (see inset in Figure S1).

**Comparison between the three methods**

In Table S1 we summarize some of the most relevant features related to the performance of each proposed method.

| | Microtransfer Molding | Microfluidic Flow Focusing | Template Assisted Electrodeposition |
|---|---|---|---|
| Typical supraparticle size (μm) | [10, 200] | [10, 100] | Diameter: 0.2<br>Length: [1, 30] |
| Max. supraparticle magnetic content | ~50 vol% | ~1 vol% | 100 vol% |
| Max. magnetic content per batch (μL) | ~20 | ~2 | ~0.5 |
| Time per batch (h) | 1 (PDMS activation) + 4 (UV exposure) + 12 (mold release) (Total = 17 h) | 6 (droplet generation) + 4 (UV exposure) (Total = 10 h) | 1 (growth in the template) + 24 (template release) (Total = 25 h) |
| Shape anisotropy | ✓ | ✗ | ✓ |
| Magnetic content anisotropy | ✓ | ✓ | ✓ |
| Monodispersity | ✓ | ✓ | ✓ |

Table S1: Summary table of the three proposed methods.

All of them allow a precise control on the particle shape, size and magnetic content distribution. Ideal maximum magnetic content obtained in one batch together with the time required to get it are also compared. For microtransfer molding, we assume that a batch is the total number of supraparticles collected from a fully covered PDMS mold

(mold diameter of approximately 10 cm). In the case of flow focusing, a batch corresponds to the number of particles synthesized until the continuous phase in the reservoir (40 mL) runs out. Note that the flow rate for the continuous phase is always larger than that of the dispersed phase (see Table 3 in the main text). Finally, in the electrodeposition technique, a batch refers to the microwires synthesized using just one alumina template (diameter smaller than 5 cm). “Batches” were defined so as to keep monodispersity as high as possible in the supraparticle population.

From Table S1, for a given synthesis time, it can be seen that microtransfer molding could be considered the best method as it allows synthesizing the largest amount of supraparticles (supposing that all wells in the mold are filled). On the contrary, electrodeposition technique seems to be worst. In its turn, it is important to note that the flow focusing technique suffers from some limitations that probably reduce its efficiency. The major one is that CI microparticles gradually settle down in the reservoir. This results in the reduction with time of the magnetic content in the dispersed phase that flows through the flow focusing device and eventually makes shorter the available time to produce supraparticles with the same magnetic content.