Different Aspect Ratio Polysaccharide-Assisted Assembling of Magnetic Nanoparticles

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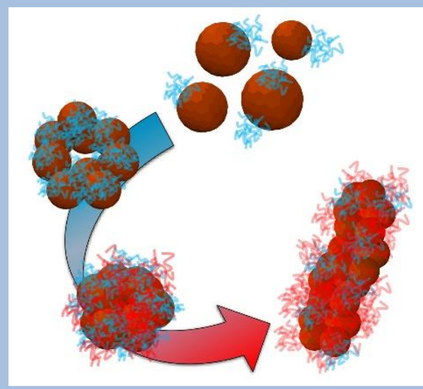
Summary

The controlled aggregation of superparamagnetic nanoparticles in superstructures, namely clustering, offers the advantage of maintaining the superparamagnetic behavior of the individual nanoparticles, while there is a faster accumulation on the magnet due to the cumulative magnetization effect of different magnetic nanoparticles in the inner core of the assembly. Usually, this type of superstructures can be obtained through a destabilization process of the surface coating, through the use of partially soluble / miscible organic solvents such as to cause an increase in surface tension. If the process is properly guided, an increase in size and a control over the three-dimensional structure are obtained. Herein, versatile methods are here presented for the assembling of magnetic nanoparticles in controlled super-structures with different final aspect ratios.

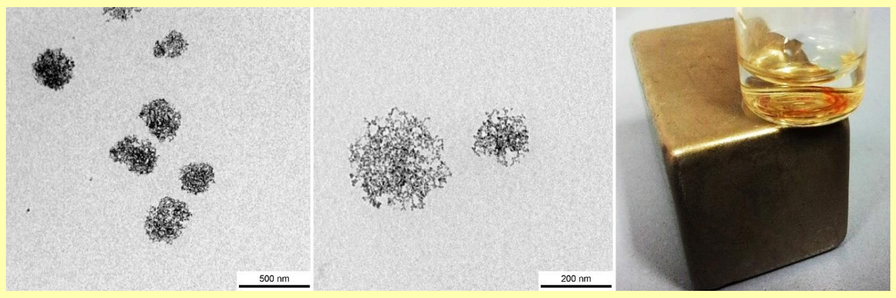


Destabilization in tube and in device

Starting from dextran-coated magnetic nanoparticles as building blocks, the clustering was induced in a tube reaction by controlled addition of a polar aprotic solvent as the acetonitrile (ACN), obtaining spherical magnetic clusters (SMC). It was found that the variations in volume and flow rate of the destabilizing agent deeply affect the destabilization process of magnetic nanoparticles. Moreover, an improvement in the stability of the superstructures was achieved by introducing an additional chitosan coating, diluting the polysaccharide in an ACN solution possessing a percentage slightly higher than that used for the destabilization step. (Figure 1).

The interest was then essentially focused on the possible effect that the fluid-dynamic processes at the interface, which occur at the microscale, can have on the control of the destabilization of magnetic nanoparticles. Our results demonstrated that a microfluidic device could be exploited as an effective tool for controlling NP aggregation process and rearrange magnetic clusters with improved magnetic properties (Figure 2). In the device the mixing time of solvents was controllable and tunable, opening new strategies to synthesize nanomaterials with more precise dimensions at narrow size distribution (Figure 3).

Figure 1. TEM images of SMC obtained by in tube destabilization. On the right, a photograph of SMC suspension magnetically sorted in few seconds.



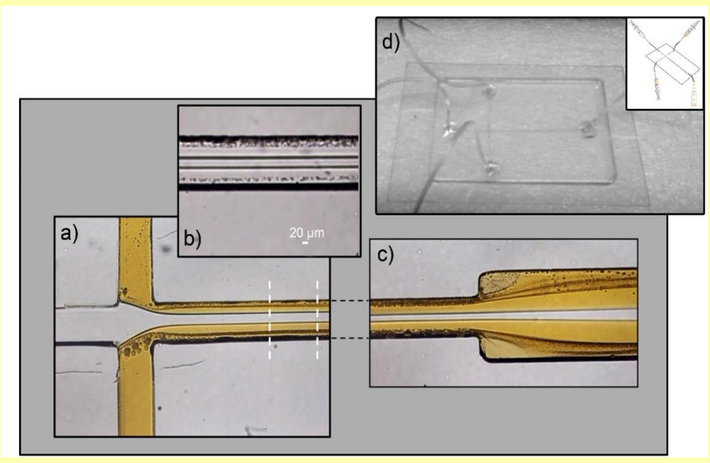


Figure 2. Detail of two different sections of the microchannel system. On the left (a-b), the cross junction near the inlet region where the laminar flow generated by the injection is observed; on the right (c), the final stretch near the outlet region, where a turbulent motion is generated. In d), a photograph and a sketch of the device are shown.

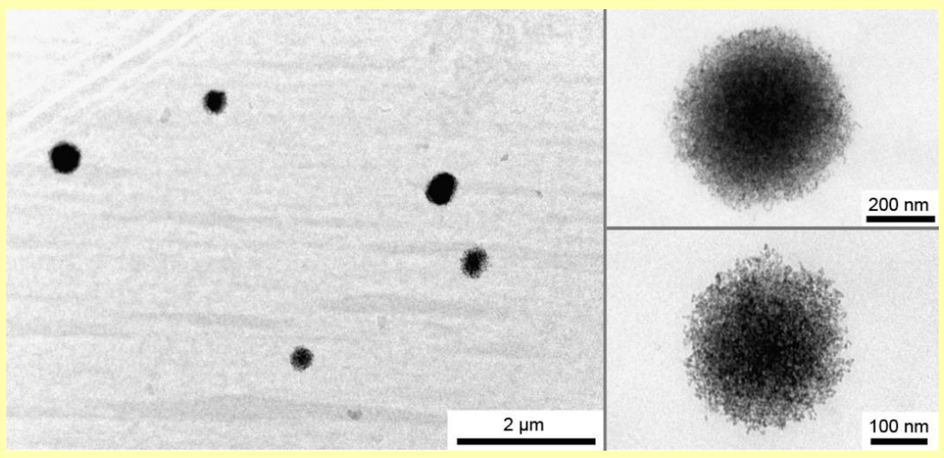


Figure 3. TEM images of SMC obtained by device destabilization. The inner nanoparticle density and the size distribution of the SMC were clearly improved by destabilizing the dextran-coated nanoparticles in a microfluidic device.

Destabilization in presence of magnetic field

The effects of the introduction of static magnetic fields (Figure 4) in the destabilization process have been evaluated for the generation of structures with a high aspect ratio. In this case, the use of superparamagnetic nanoparticles allowed, using a dilute suspension of nanocrystals, not to generate any type of aggregates until the percentage threshold of ACN is reached: the formation of the elongated magnetic structures (EMS) occurs very quickly, thus the strength and geometry of the applied magnetic field had a fundamental importance in the morphology of the superstructure. From the TEM images (Figure 5), it can be seen that an average aspect ratio value of 13 ± 4 has been obtained in the best tests with more elongated superstructures.

Figure 5. TEM images of the best EMS preparations obtained by *P* configuration (sketch in inset). In a typical experimental setup, the vial containing the nanoparticles suspension was placed close to the magnet onto an orbital shaker; the ACN was then slowly added to obtain the elongated structures. As for SMC, the EMS as prepared where then stabilized by grafting a chitosan layer to "seal" the obtained geometry.

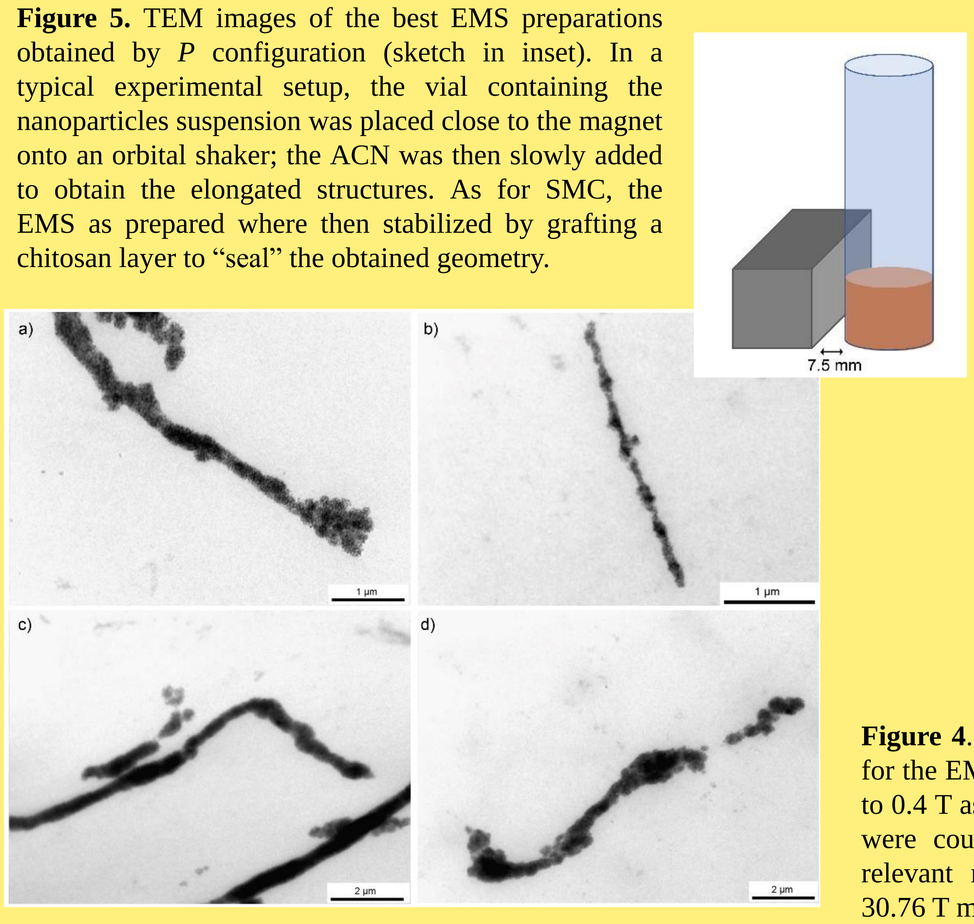


Figure 4. Photograph of the magnets used for the EMS preparation. Ranging from 0.1 to 0.4 T as nominal field, different magnets were coupled to obtain an uniform and relevant magnetic gradient fields, up to 30.76 T m^{-1} using the *P* magnet.

Conclusions

The presented methodology and reported experimental findings focus on different possible approaches for the super-assembly of magnetic nanocrystals, basing the clustering procedure on the controlled destabilization of dextran-coated nanoparticles. By exploiting the high biocompatibility of all the components used, these destabilization and/or stabilization approaches through the use of paired polysaccharides can be used for multiple applications in the medical field.

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